Supporting Information

Pure Hydrocarbon Materials as Highly Efficient Host for White Phosphorescent Organic Light-Emitting Diodes: A New Molecular Design Approach

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1 Experimental methods

1.1 General Information

All reactions were performed under a nitrogen atmosphere unless otherwise stated. Dry tetrahydrofuran (THF) was purified by PURE SOLV (Innovative Technology) purification system. $^1$H NMR was recorded in chloroform-$d$ (CDCl$_3$) on a Bruker 400 MHz at room temperature. Matrix-Assisted Laser Desorption/Ionization Time of Flight Mass Spectrometry (MALDI-TOF-MS) was measured with a Bruker ultraflexextreme MALDI-TOF spectrometer. UV-visible spectra were recorded using an UV-vis spectrophotometer (Lambda 750) in toluene. Molar absorption coefficients ($\varepsilon$) were calculated from the gradients extracted from the plots of absorbance vs concentration with five solutions of different concentrations for each sample. The fluorescent and phosphorescent (liquid nitrogen) spectra were tested by Hitachi F-4600 spectrophotometer, both in toluene solution. The excitation wavelength was 290 nm for both, modulated by a monochromator. Triplet energy levels were calculated from the maximum of the first phosphorescence emission peak, and conversion in electron-volt was obtained with the following formula: $E_T (eV) = \frac{hc}{\lambda}$ with $h = 6.62607 \times 10^{-34}$ J.s, $c = 2.99792 \times 10^{17}$ nm s$^{-1}$ and 1 J = 6.24151$\times$10$^{18}$ eV. This equation can be simplified as: $\langle eV \rangle = \frac{1239.84}{\lambda}$ with $\lambda$ formulated in nm. The transient decay PL characteristics were evaluated using a HAMAMATSU (C11637) compact fluorescence lifetime spectrometer under an excitation light wavelength of 373 nm.

1.2 X-Ray analysis

Crystals were picked up with a cryoloop and then frozen at 150 K or 170 K under a stream of dry N$_2$. Data were collected on a D8 VENTURE Bruker AXS diffractometer with Mo–K$\alpha$ radiation ($\lambda = 0.71073$ Å).

Structures were solved by direct methods (SIR92)$^1$ and refined (SHELXL-2014/7)$^2$ by full-matrix least-squares methods as implemented in the WinGX software package.$^3$ An empirical absorption (multi-scan) correction was applied. Hydrogen atoms were introduced at calculated positions (riding model) included in structure factor calculation but not refined. Refinement parameters are summarized in Tables S1 and S2.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication data: **1-mtp-SBF** (CCDC 2142857) **1-mbp-SBF** (CCDC 2168574) and **1-p-SBF** (CCDC 1495896).$^4$ Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax:
1.3 Electrochemical analysis

Electrochemical experiments were performed under an argon atmosphere using a Pt disk electrode (diameter 1 mm). The counter electrode was a vitreous carbon rod. The reference electrode was either a silver wire in a 0.1 M AgNO₃ solution in CH₃CN for the studies in oxidation or a silver wire coated by a thin film of AgI (silver(I)iodide) in a 0.1 M Bu₄NI solution in DMF for the studies in reduction. Ferrocene was added to the electrolyte solution at the end of a series of experiments. The ferrocene/ferrocenium (Fc/Fc⁺) couple served as an internal standard. The three electrodes cell was connected to a potentiostat/galvanostat (Autolab/PGSTAT101) monitored with the Nova 2.1 Software. Activated Al₂O₃ was added to the electrolytic solution to remove excess moisture. For further comparison, all potentials are referred to the SCE electrode that was calibrated at -0.405 V vs. Fc/Fc⁺ system. We estimated the electron affinity (EA) or the lowest unoccupied molecular orbital (LUMO) and the ionization potential (IP) or the highest occupied molecular orbital (HOMO) from the redox data. The LUMO level was calculated from the cyclic voltammetry in reduction recorded in DMF (+ Bu₄NPF₆ 0.1 M) as follow: LUMO (eV) = - [E_onset_red (vs SCE) + 4.4]. Similarly the HOMO level was calculated from the cyclic voltammetry in oxidation recorded in CH₂Cl₂ (+ Bu₄NPF₆ 0.2 M) as follow: HOMO (eV) = - [E_onset_ox (vs SCE) + 4.4] based on an SCE energy level of 4.4 eV relative to the vacuum. The electrochemical gap was calculated from: ΔE_elec = |HOMO-LUMO| (eV).

1.4 Molecular modeling

Full geometry optimization of the ground state (S₀) and frequency calculation were performed with Density Functional Theory (DFT)⁵-⁶ using the hybrid Becke-3 0 parameter exchange functional⁷-⁸ and the Lee-Yang-Parr non-local correlation functional⁹ (B3LYP) implemented in the Gaussian 16 (Revision B.01) program suite using the 6-31G(d) basis set and the default convergence criterion implemented in the program. Geometry optimization of the first excited triplet state (E₅₁) was performed using Time-Dependent-Density Functional Theory (TD-DFT) calculations using the B3LYP functional and the 6-31+G(d) basis set. Infrared spectra were calculated on the final geometry to verify that an energy minimum was reached (i.e. no negative frequency). Transition diagrams were obtained through TD-DFT calculations performed using the
M06-2X functional and the extended 6-311+G(d, p) basis set on the geometry of S0. T1 to S0 energy transition (E_T) was calculated from the difference between the total energy of the molecule in its respective excited triplet state (found through TD-DFT, B3LYP 6-311+G(d, p)) and its ground singlet state (found through DFT, B3LYP 6-311+G(d, p)) in their optimized geometries.

Spin density (SD) representation was obtained through TD-DFT calculations performed using the extended 6-311+G(d, p) basis set and a triplet spin on the previously optimized geometry of T1.

Calculations were carried out on the OCCIGEN calculator of the Centre Informatique National de l'Enseignement Supérieur (CINES (Montpellier) under project No. 2021-A0100805032). Figures were generated with GaussView 6.0 and GaussSum 3.0.

### 1.5 Thermal analysis

Thermal Gravimetric Analysis (TGA) was carried out by using a METTLER TOLEDO TGA1 instrument. TGA curves were measured at 10 °C min⁻¹ from 30 °C to 700 °C under nitrogen flux. Differential Scanning Calorimetry (DSC) was carried out by using a METTLER TOLEDO DSC1 unit instrument equipped with an intracooler. DSC traces were measured at 10 °C min⁻¹, 2 heating/cooling cycles were successively carried out under nitrogen flux.

### 1.6 Device fabrication and characteristics

All organic compounds except the product of this paper were purchased from Lumtec Co., Ltd. ITO substrates (185 nm, R = 10 Ω/square for blue PhOLEDs, 135 nm, R = 15 Ω/square for white PhOLEDs; activating area 0.1 cm²; glass substrate, 32 mm × 32 mm × 0.7 mm) with patterned electrodes were ultrasonically cleaned in deionized water, acetone and ethanol for 15 min. Before loading into the vacuum chamber, the substrates were treated by UV ozone for 15 min at 40 °C. OLED devices were fabricated by depositing materials in a thermal evaporator chamber under a vacuum of 4.0 × 10⁻⁶ Torr. The organic layers and cathode were defined by shallow masks placed under the substrates (0.15 cm²), which define an active area of 0.1 cm². The evaporation rates and thicknesses of organic layers (2–4 Å s⁻¹) and aluminum cathode (4–8 Å s⁻¹) were monitored with oscillating quartz crystals. The devices were well encapsulated with glued glass lids before testing. A programmable spectra scan photometer (PHOTO RESEARCH, PR 655) connected to a KEITHLEY 2400 source meter was used to test the EL and luminescence characteristics, and the current–voltage characteristics.
2 Syntheses of materials

2.1 1-Phenyl-9,9'-spirobifluorene [1-p-SBF]\(^4\)

The synthesis and characterization of 1-p-SBF can be found in previous works.\(^4\)

2.2 1-Biphenyl-9,9'-spirobifluorene [1-mbp-SBF]

A mixture of compound 1 (2.00 g, 7.75 mmol), [1,1'-biphenyl]-3-ylboronic acid (1.84 g, 9.29 mmol), K\(_2\)CO\(_3\) (2.13 g, 15.43 mmol) and Pd(PPh\(_3\))\(_4\) (0.89 g, 0.77 mmol) in 100 mL THF with distilled water (10 mL) was stirred for 24 hours at 80 °C under a nitrogen atmosphere. After it was cooled to room temperature, the mixture was extracted with dichloromethane (DCM, 3 x 45 mL), and the combined organic layer was dried over anhydrous MgSO\(_4\). The solvent was removed off by rotary evaporation and the silica gel column was used to pass the residue with petroleum ether (PE)/ DCM (v/v, 7:3) as an eluent to obtain compound 1-([1,1'-biphenyl]-3-yl)-9H-fluoren-9-one as yellow solid (2.25 g, 87.54%). \(^1\)H NMR (400 MHz, Chloroform-d) \(\delta\) 7.77 (p, J = 1.0 Hz, 1H), 7.71 – 7.60 (m, 4H), 7.59 – 7.51 (m, 5H), 7.51 – 7.42 (m, 3H), 7.38 – 7.26 (m, 3H). \(^13\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 193.02, 145.59, 143.56, 142.17, 141.22, 140.87, 137.81, 134.51, 134.26, 131.66, 129.78, 129.24, 128.76, 128.32, 128.24, 128.08, 127.37, 127.28, 127.06, 124.20, 120.03, 119.33. MALDI-MS (m/z) of C\(_{25}\)H\(_{16}\)O for [M\(^+\)]: calcd. 332.12; found, 332.68. Anal. calcd for C\(_{25}\)H\(_{16}\)O (%): C, 90.33; H, 4.85; O, 4.81; found: C, 90.24; H, 4.89; O 4.87.
Compound 2-bromo-1,1'-biphenyl (2.94 g, 12.65 mmol) was dissolved in 60 mL THF in a 200 mL Schlenk tube under argon. After the solution was cooled to -78 °C, 1.6 M n-BuLi (9.48 mL, 15.18 mmol) was added drop by drop in 10 minutes. The resulting mixture was allowed to stir for 1 hour at -78 °C, and then 1-[(1,1'-biphenyl)-3-yl]-9H-fluoren-9-one (3.5 g, 10.54 mmol) was added. After, the mixture was stirred at room temperature overnight. 10 mL distilled water was added to the mixture to quench the reaction and THF was evaporated under reduced pressure. The resulting solid was dissolved in 100 mL DCM and washed with water (3 × 50 mL). Then the organic layer was separated, dried with sodium sulfate, filtered, and evaporated, resulting in the white solid, which was directly used in the next reaction without further purification. The crude product was dissolved in 40 mL AcOH and 5 mL HCl (36%) at 110 °C for 4 hours under stirring. After the reaction was cooled to room temperature, the mixture was poured into ice water and filtered to get the crude product. The resulting solid was further purified by column chromatography using PE/DCM (v/v, 4:1) as eluent to afford a white powder (4.18 g, 84.92%). 1H NMR (400 MHz, Chloroform-d) δ 7.96 – 7.82 (m, 2H), 7.45 (t, J = 7.6 Hz, 1H), 7.37 – 7.26 (m, 6H), 7.22 – 7.11 (m, 3H), 7.11 – 6.96 (m, 6H), 6.82 – 6.68 (m, 3H), 6.58 (d, J = 7.6 Hz, 1H), 6.40 (t, J = 1.7 Hz, 1H), 6.15 – 6.06 (m, 1H). 13C NMR (101 MHz, Chloroform-d) δ 149.30, 148.13, 145.45, 142.46, 141.97, 141.23, 141.03, 139.11, 129.24, 128.27, 128.89, 128.79, 127.50, 127.40, 127.31, 127.16, 126.87, 126.80, 124.52, 123.78, 123.67, 119.97, 119.74, 119.02. MALDI-MS (m/z) of C37H24 for [M]+: calcd. 468.19; found, 468.63. Anal. calcd for C37H24 (%): C, 94.84; H, 5.16; found: C, 94.81; H, 5.19. Melting range: 179.6-179.7 °C.

2.3 1-Terphenyl-9,9'-spirobifluorene [1-mtp-SBF]
A mixture of compound 1 (3.00 g, 11.63 mmol), [1,1′:3′,1″-terphenyl]-5′-ylboronic acid (3.50 g, 12.77 mmol), K₂CO₃ (3.21 g, 23.26 mmol) and Pd(PPh₃)₄ (1.34 g, 1.16 mmol) in 100 mL THF was stirred for 24 hours at 80 °C under a nitrogen atmosphere. After it was cooled to room temperature, the mixture was extracted with dichloromethane (DCM, 3 × 45 mL), and the combined organic layer was dried over anhydrous MgSO₄. The solvent was removed off by rotary evaporation and the silica gel column was used to pass the residue with PE/ DCM (v/v, 7:3) as an eluent to obtain compound 1-([1,1′:3′,1″-terphenyl]-5′-yl)-9H-fluoren-9-one as yellow solid (4.62 g, 88.58%).

\[ \begin{align*}
\text{H NMR (400 MHz, Chloroform-d)} & \quad \delta 7.86 (t, J = 1.7 Hz, 1H), 7.79 – 7.70 (m, 6H), 7.65 (dt, J = 7.3, 0.9 Hz, 1H), 7.61 – 7.54 (m, 3H), 7.54 – 7.51 (m, 1H), 7.50 – 7.43 (m, 4H), 7.40 – 7.29 (m, 4H). \\
\text{C NMR (101 MHz, Chloroform-d)} & \quad \delta 145.67, 143.56, 142.05, 141.42, 141.21, 138.17, 134.52, 134.30, 131.70, 129.26, 128.79, 127.47, 127.41, 127.22, 126.07, 124.26, 120.04, 119.42, 77.23. \\
\text{MALDI-MS (m/z) of C}_{31}H_{20}O for [M]⁺: calcd. 408.15; found, 408.72. \\
\text{Anal. calcd for C}_{31}H_{20}O (%): C, 91.15; H, 4.94; O, 3.92; found: C, 91.28; H, 4.88; O, 3.84. }
\end{align*} \]

Compound 2-bromo-1,1′-biphenyl (2.32 g, 10.00 mmol) was dissolved in 60 mL THF in a 200 mL Schlenk tube underargon. After the solution was cooled to -78 °C, 1.6 M n-BuLi (7.56 mL, 12.00 mmol) was added drop by drop in 10 minutes. The resulting mixture was allowed to stir for 1 hour at -78 °C, and then 1-([1,1′:3′,1″-terphenyl]-5′-yl)-9H-fluoren-9-one (3.00 g, 7.35 mmol) was added. After, the mixture was stirred at room temperature overnight. 10 mL distilled water was added to the mixture to quench the reaction and THF was evaporated under reduced pressure. The resulting solid was dissolved in 100 mL DCM and washed with water (3 × 50 mL). Then the organic layer was separated, dried with sodium sulfate, filtered and evaporated, resulting in the white solid, which was directly used in the next reaction without further purification. The crude product was dissolved in 40 mL AcOH and 5 mL HCl (36%) at 110 °C for 4 hours under stirring. After the reaction was cooled to room temperature, the mixture was poured into ice water and filtered to get crude product. The resulting solid was further purified by column chromatography using PE/ DCM (v/v, 4:1) as eluent to afford a white powder (3.46 g, 85.91%).

\[ \begin{align*}
\text{H NMR (400 MHz, Chloroform-d)} & \quad \delta 7.94 – 7.84 (m, 2H), 7.47 (t, J = 7.6 Hz, 1H), 7.40 – 7.32 (m, 6H), 7.32 – 7.27 (m, 2H), 7.26 (d, J = 1.8 Hz, 3H), 7.24 (d, J = 1.4 Hz, 1H), 7.20 – 7.16 (m, 2H), 7.05 (td, J = 7.5, 1.1 Hz, 2H), 6.96 (td, J = 7.4, 1.2 Hz, 2H), 6.86 (td, J = 7.5, 1.1 Hz, 2H), 6.78 (dd, J = 7.5, 1.0 Hz,} \]
2H), 6.56 (dd, \( J = 7.6 \), 1.0 Hz, 1H), 6.38 (dd, \( J = 1.7 \), 0.6 Hz, 2H). \(^{13}\)C NMR (101 MHz, Chloroform-\( d_2 \)) \( \delta \) 148.00, 141.90, 141.19, 140.99, 140.44, 140.08, 139.56, 129.20, 128.34, 127.91, 127.85, 127.51, 127.41, 127.24, 127.09, 126.97, 126.62, 123.77, 123.62, 123.57, 119.99, 119.66, 119.12. MALDI-MS (m/z) of \( \text{C}_{43}\text{H}_{28} \) for [M\(^+\)]: calcd. 544.22; found, 544.89. Anal. calcd for \( \text{C}_{43}\text{H}_{28} \) (%): C, 94.82, H, 5.18; found: C, 94.93; H, 5.07. Melting range: 182.8-182.9 °C.

2.4 1-Quaterphenyl-9,9'-spirobifluorene [1-mqp-SBF]

1-Quaterphenyl-9-fluorenone 4,4,5,5-tetramethyl-2-(5'-phenyl-[1,1':3',1''-terphenyl]-3-yl)-1,3,2-dioxaborolane was synthesized using a previously reported synthetic procedure. \(^{10}\) 1-Bromo-9H-fluoren-9-one (0.800 g, 3.09 mmol, 1.0 eq), 4,4,5,5-tetramethyl-2-(5'-phenyl-[1,1':3',1''-terphenyl]-3-yl)-1,3,2-dioxaborolane (1.60 g, 371 mmol, 1.4 eq), potassium carbonate (2.13 g, 15.4 mmol, 5.0 eq), [1,1'-bis(diphenylphosphino)ferrocene]dichloropalladium(II) (0.226 g, 0.309 mmol, 0.1 eq) were dissolved in dry DMF (26 mL) under an argon atmosphere. The resulting mixture was refluxed for 24 h. After cooling to room temperature, a saturated solution of ammonium chloride was added. The crude product was extracted with CH\(_2\)Cl\(_2\), washed with water, dried over MgSO\(_4\), filtered and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel [column conditions: silica cartridge (40 g); solid deposit on Celite®; \( \lambda \) detection: (254 nm, 280 nm); CH\(_2\)Cl\(_2\)/light petroleum (from 1/9 to 2/8) at 40 mL/min], giving the title compound as a yellow solid (1.08 g, 2.23 mmol); yield 72%. \(^{1}\)H NMR (400 MHz, CD\(_2\)Cl\(_2\)) \( \delta \) 7.91 (d, \( J = 1.7 \) Hz, 3H), 7.84 (t, \( J = 1.7 \) Hz, 1H), 7.80 (dt, \( J = 6.6 \), 2.2 Hz, 1H), 7.77 – 7.73 (m, 4H), 7.64 – 7.47 (m, 11H), 7.42 – 7.37 (m, 2H), 7.33 (ddd, \( J = 7.6 \), 5.5, 1.2 Hz, 2H). \(^{13}\)C NMR (101 MHz, CD\(_2\)Cl\(_2\)) \( \delta \) 192.83, 145.57, 143.50, 142.33, 142.16, 141.77, 141.03, 140.60, 138.18, 134.54, 134.31, 134.22, 131.57, 129.81, 129.23, 128.83, 128.42, 128.39, 127.56, 127.29, 126.99, 125.15, 125.09, 123.92, 120.12, 119.49. ASAP (m/z) calculated for \( \text{C}_{37}\text{H}_{25}\text{O} \) [M+H]+: 485.190, found: 485.190.
2-Iodo-1,1'-biphenyl (1.16 g, 0.413 mol, 2.0 eq) was dissolved in dry THF (50 mL) under argon and the mixture was cooled to -78°C. n-BuLi (2.50 M in hexanes, 2.06 mL, 0.516 mol, 2.5 eq) was then added dropwise and the resulting mixture was stirred for 30 min. 1-mqp-9H-fluoren-9-one (1.079 g, 0.206 mol, 1.0 eq) was dissolved under argon in dry THF (25 mL) and added dropwise to the reaction mixture and stirred for 30 additional minutes. Then, the reaction was allowed to warm up to room temperature under stirring overnight. The reaction mixture was quenched with a few drops of absolute ethanol and then the solvent was removed under reduced pressure. The crude was dried under a vacuum at 60°C overnight. Without further purification, the crude was dissolved in acetic acid (100 mL) and hydrochloric acid (10 mL) was added under stirring. The reaction mixture was refluxed overnight under stirring. After cooling to room temperature, water was added to the reaction mixture and the crude was extracted with CH$_2$Cl$_2$. The combined organic layers were washed with NaHCO$_3$ saturated solution till neutral, washed with water, dried over MgSO$_4$, filtered and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel [column conditions: silica cartridge (80 g); solid deposit on Celite®; λ detection: (254 nm, 280 nm); CH$_2$Cl$_2$/light petroleum (from 1/9 to 2/8) at 60 mL/min], giving the title compound as a white solid (0.970 g, 0.674 mol); yield 76 %; $^1$H NMR (400 MHz, CD$_2$Cl$_2$) δ 7.93 (dd, $J = 9.2, 7.7$ Hz, 2H), 7.77 – 7.68 (m, 5H), 7.50 (m, $J = 7.3$ Hz, 5H), 7.43 – 7.34 (m, 5H), 7.29 (m, $J = 11.6, 5.7, 2.0$ Hz, 3H), 7.10 – 6.96 (m, 6H), 6.82 – 6.71 (m, 3H), 6.52 (m, $J = 4.5, 2.6$ Hz, 2H), 6.19 – 6.15 (d, 1H). $^{13}$C NMR (101 MHz, CD$_2$Cl$_2$) δ 149.33, 148.19, 142.51, 142.05, 142.01, 141.93, 141.29, 141.15, 140.54, 139.33, 129.26, 128.78, 127.87, 127.84, 127.75, 127.55, 127.49, 127.37, 127.27, 127.20, 127.02, 124.98, 124.62, 123.50, 123.44, 120.12, 119.82, 119.15, 65.88. MALDI (m/z) calculated for C$_{49}$H$_{32}$ [M]+: 620.249, found: 620.250.
3 X-Ray studies

Table S1. Crystal data and structure refinement for 1-mbp-SBF.

| Property                        | Value                                      |
|---------------------------------|--------------------------------------------|
| Empirical formula               | C_{37}H_{24}                               |
| Formula weight                  | 468.56                                     |
| Temperature/K                   | 170.0                                      |
| Crystal system                  | Triclinic                                  |
| Space group                     | P-1                                        |
| Unit cell dimensions            | a/Å: 9.8641(3), b/Å: 11.4538(4), c/Å: 12.4640(4), ω/°: 102.9530(10), β/°: 109.3830(10), γ/°: 100.2050(10) |
| Volume/ Å³                      | 1245.17(7)                                 |
| Z                               | 2                                          |
| Density/g/cm³                   | 1.250                                      |
| Absorption coefficient/mm⁻¹     | 0.071                                      |
| F(000)                          | 492.0                                      |
| Crystal size/mm³                | 0.29 × 0.19 × 0.15                         |
| Theta range for data collection/°| 4.596 to 52.85                             |
| Index ranges                    | -12 ≤ h ≤ 12                               |
|                                 | -14 ≤ k ≤ 14                               |
|                                 | -15 ≤ l ≤ 14                               |
| Reflections collected           | 14428                                      |
| Independent reflections         | 5084 [R_{int} = 0.0547, R_{sigma} = 0.0617]|
| Data/restraints/parameters      | 5084/0/334                                 |
| Goodness-of-fit on F²            | 1.031                                      |
| Final R indices [I>2sigma(I)]   | R₁ = 0.0464, wR₂ = 0.1012                  |
| R indices (all data)            | R₁ = 0.0678, wR₂ = 0.1167                  |
| Largest diff. peak and hole     | 0.23/-0.17                                 |
| Radiation                       | MoKα (λ = 0.71073)                         |
| CCDC number                     | 2168574                                    |

Table S2. Crystal data and structure refinement for 1-mtp-SBF.

| Property                        | Value                                      |
|---------------------------------|--------------------------------------------|
| Empirical formula               | C_{43}H_{28}                               |
| Formula weight                  | 544.65                                     |
| Temperature/K                   | 150.0                                      |
| Crystal system                  | Monoclinic                                 |
| Space group                     | P 21/c                                     |
| Unit cell dimensions            | a/Å: 15.1812(13)                           |
| Property                              | Value                                  |
|--------------------------------------|----------------------------------------|
| b/Å:                                 | 14.3062(12)                            |
| c/Å:                                 | 14.5694(12)                            |
| α/°:                                 | 90                                     |
| β/°:                                 | 111.095(2)                             |
| γ/°:                                 | 90                                     |
| Volume/ Å³                           | 2952.2(4)                              |
| Z                                     | 4                                      |
| Density/g/cm³                        | 1.225                                  |
| Absorption coefficient/mm⁻¹          | 0.069                                  |
| F(000)                               | 1144                                   |
| Crystal size/mm³                     | 0.38 × 0.23 × 0.11                     |
| Theta range for data collection/°     | 2.809 to 27.489                        |
| Index ranges                         | -19 ≤ h ≤ 17                           |
|                                      | -18 ≤ k ≤ 18                           |
|                                      | -17 ≤ l ≤ 18                           |
| Reflections collected                | 24776                                  |
| Independent reflections              | 6723 [R_int = 0.0324]                  |
| Data/restraints/parameters           | 6723/0/388                             |
| Goodness-of-fit on F²                | 1.017                                  |
| Final R indices [I>2sigma(I)]        | R₁ = 0.0424, wR₂ = 0.0928              |
| R indices (all data)                 | R₁ = 0.0711, wR₂ = 0.1062              |
| Largest diff. peak and hole          | 0.237/-0.213                           |
| Radiation                            | MoKα (λ = 0.71073)                     |
| CCDC number                          | 2142857                                |
Table S3. Atomic coordinates (x $10^4$) and equivalent isotropic displacement parameters ($\AA^2 x 10^3$) for 1-mbp-SBF. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

|     | x     | y     | z     | U(eq) |
|-----|-------|-------|-------|-------|
| C(1)| 6283(1)| 7682(1)| 2801(1)| 14(1) |
| C(2)| 7289(1)| 7990(1)| 2145(1)| 15(1) |
| C(3)| 8430(1)| 7481(1)| 2038(1)| 19(1) |
| C(4)| 9226(1)| 7919(1)| 1403(1)| 22(1) |
| C(5)| 8893(1)| 8854(1)| 900(1) | 22(1) |
| C(6)| 7766(1)| 9383(1)| 1024(1)| 20(1) |
| C(7)| 6954(1)| 8937(1)| 1646(1)| 16(1) |
| C(8)| 5697(1)| 9278(1)| 1896(1)| 16(1) |
| C(9)| 4952(1)| 10149(1)| 1576(1)| 20(1) |
| C(10)| 3736(1)| 10243(1)| 1886(1)| 21(1) |
| C(11)| 3271(1)| 9477(1)| 2489(1)| 19(1) |
| C(12)| 4013(1)| 8596(1)| 2821(1)| 15(1) |
| C(13)| 5249(1)| 8521(1)| 2531(1)| 14(1) |
| C(14)| 5476(1)| 6306(1)| 2454(1)| 15(1) |
| C(15)| 4514(1)| 5514(1)| 1335(1)| 20(1) |
| C(16)| 3846(2)| 4291(1)| 1236(1)| 26(1) |
| C(17)| 4118(2)| 3893(1)| 2244(1)| 27(1) |
| C(18)| 5105(2)| 4679(1)| 3364(1)| 23(1) |
| C(19)| 5808(1)| 5887(1)| 3461(1)| 16(1) |
| C(20)| 6917(1)| 6904(1)| 4498(1)| 16(1) |
| C(21)| 7697(2)| 6933(1)| 5668(1)| 23(1) |
| C(22)| 8763(2)| 8029(1)| 6457(1)| 26(1) |
| C(23)| 9033(2)| 9080(1)| 6093(1)| 24(1) |
| C(24)| 8236(1)| 9060(1)| 4929(1)| 19(1) |
| C(25)| 7195(1)| 7962(1)| 4135(1)| 15(1) |
| C(26)| 3405(1)| 7790(1)| 3440(1)| 16(1) |
| C(27)| 3868(2)| 8166(1)| 4677(1)| 26(1) |
| C(28)| 3161(2)| 7474(1)| 5218(1)| 33(1) |
| C(29)| 1989(2)| 6414(1)| 4538(1)| 27(1) |
| C(30)| 1511(1)| 6006(1)| 3294(1)| 18(1) |
| C(31)| 2248(1)| 6703(1)| 2764(1)| 16(1) |
| C(32)| 213(1)| 4902(1)| 2545(1)| 18(1) |
| C(33)| 130(2)| 4133(1)| 1466(1)| 24(1) |
| C(34)| -1124(2)| 3141(1)| 747(1)| 29(1) |
| C(35)| -2323(2)| 2899(1)| 1083(1)| 29(1) |
| C(36)| -2251(2)| 3644(1)| 2155(1)| 29(1) |
| C(37)| -1000(2)| 4631(1)| 2878(1)| 24(1) |
Table S4. Bond lengths [Å] and angles [°] for 1-mbp-SBF.

| Bond | Length/Angle | Bond | Length/Angle |
|------|--------------|------|--------------|
| C(1)-C(2)  | 1.5252(16)  | C(34)-C(35) | 1.386(2)  |
| C(1)-C(14) | 1.5260(16)  | C(17)-C(18)-C(19) | 118.51(12) |
| C(1)-C(25) | 1.5307(15)  | C(17)-C(18)-H(18) | 120.7 |
| C(1)-C(13) | 1.5312(16)  | C(19)-C(18)-H(18) | 120.7 |
| C(2)-C(3)  | 1.3872(17)  | C(18)-C(19)-C(14) | 120.28(11) |
| C(2)-C(7)  | 1.4022(16)  | C(18)-C(19)-C(20) | 131.02(12) |
| C(3)-C(4)  | 1.3951(18)  | C(14)-C(19)-C(20) | 108.71(10) |
| C(3)-H(3)  | 0.9500      | C(21)-C(20)-C(25) | 120.27(11) |
| C(4)-C(5)  | 1.3926(19)  | C(21)-C(20)-C(19) | 131.23(11) |
| C(4)-H(4)  | 0.9500      | C(25)-C(20)-C(19) | 108.44(10) |
| C(5)-C(6)  | 1.3928(19)  | C(22)-C(21)-C(19) | 118.67(12) |
| C(5)-H(5)  | 0.9500      | C(22)-C(21)-H(21) | 120.7 |
| C(6)-C(7)  | 1.3973(17)  | C(20)-C(21)-H(21) | 120.7 |
| C(6)-H(6)  | 0.9500      | C(23)-C(22)-C(19) | 120.83(12) |
| C(7)-C(8)  | 1.4700(17)  | C(23)-C(22)-C(21) | 119.6 |
| C(8)-C(9)  | 1.3923(17)  | C(23)-C(22)-H(22) | 119.6 |
| C(8)-C(13) | 1.4069(16)  | C(21)-C(22)-H(22) | 120.65(12) |
| C(9)-C(10) | 1.3920(18)  | C(22)-C(23)-C(24) | 119.7 |
| C(9)-H(9)  | 0.9500      | C(22)-C(23)-H(23) | 119.7 |
| C(9)-H(9)  | 0.9500      | C(24)-C(23)-H(23) | 118.55(12) |
| C(10)-C(11)| 1.3895(18)  | C(25)-C(24)-C(23) | 120.7 |
| C(10)-H(10)| 0.9500      | C(25)-C(24)-H(24) | 120.7 |
| Bond               | Distance | Angle      | Torsion | Bond               | Distance | Angle      | Torsion |
|--------------------|----------|------------|---------|--------------------|----------|------------|---------|
| C(11)-C(12)        | 1.4052(17) | C(3)-C(4)-H(4) | 119.6  | C(24)-C(25)-C(20) | 121.01(11) | C(24)-C(25)-C(1) | 128.14(11) |
| C(11)-H(11)        | 0.9500   | C(4)-C(5)-C(6) | 120.90(12) | C(24)-C(25)-C(1) | 110.77(10) | C(20)-C(25)-C(1) | 119.17(11) |
| C(12)-C(13)        | 1.3943(16) | C(4)-C(5)-H(5) | 119.5  | C(27)-C(26)-C(31) | 120.96(11) | C(27)-C(26)-C(12) | 119.55(10) |
| C(12)-C(26)        | 1.4976(16) | C(6)-C(5)-H(5) | 119.5  | C(27)-C(26)-C(12) | 119.79(12) | C(28)-C(27)-C(12) | 120.1 |
| C(14)-C(15)        | 1.3857(17) | C(5)-C(6)-C(7) | 118.46(12) | C(31)-C(26)-C(31) | 119.17(11) | C(28)-C(27)-C(12) | 120.1 |
| C(14)-C(19)        | 1.4028(17) | C(5)-C(6)-H(6) | 120.8  | C(28)-C(27)-C(12) | 120.65(13) | C(29)-C(28)-C(12) | 119.7 |
| C(15)-C(16)        | 1.3989(18) | C(7)-C(6)-H(6) | 120.8  | C(29)-C(28)-C(12) | 119.7 |
| C(15)-H(15)        | 0.9500   | C(6)-C(7)-C(2) | 120.34(11) | C(29)-C(28)-C(12) | 119.7 |
| C(16)-C(17)        | 1.391(2)  | C(6)-C(7)-C(8) | 131.06(11) | C(29)-C(28)-C(12) | 119.7 |
| C(16)-H(16)        | 0.9500   | C(2)-C(7)-C(8) | 108.59(10) | C(29)-C(28)-C(12) | 119.7 |
| C(17)-C(18)        | 1.391(2)  | C(9)-C(8)-C(13) | 121.01(11) | C(29)-C(28)-C(12) | 119.7 |
| C(17)-H(17)        | 0.9500   | C(9)-C(8)-C(13) | 130.32(11) | C(29)-C(28)-C(12) | 119.7 |
| C(18)-C(19)        | 1.3928(17) | C(13)-C(8)-C(7) | 108.64(10) | C(29)-C(28)-C(12) | 119.7 |
| C(18)-H(18)        | 0.9500   | C(10)-C(9)-C(8) | 118.39(11) | C(29)-C(28)-C(12) | 119.7 |
| C(19)-C(20)        | 1.4702(16) | C(10)-C(9)-H(9) | 120.8  | C(28)-C(29)-C(30) | 119.6 |
| C(20)-C(21)        | 1.3951(17) | C(8)-C(9)-H(9) | 120.8  | C(28)-C(29)-C(30) | 119.6 |
| C(20)-C(25)        | 1.4001(16) | C(11)-C(10)-C(9) | 120.68(11) | C(28)-C(29)-C(30) | 119.6 |
| C(21)-C(22)        | 1.3938(19) | C(11)-C(10)-H(10) | 119.7  | C(28)-C(29)-C(30) | 119.6 |
| C(21)-H(21)        | 0.9500   | C(9)-C(10)-H(10) | 119.7  | C(26)-C(31)-C(30) | 119.1 |
| C(22)-C(23)        | 1.393(2)  | C(10)-C(11)-C(12) | 121.64(12) | C(26)-C(31)-C(30) | 119.1 |
| C(22)-H(22)        | 0.9500   | C(10)-C(11)-H(11) | 119.2  | C(30)-C(31)-C(30) | 119.1 |
| C(23)-C(24)        | 1.3952(18) | C(12)-C(11)-H(11) | 119.2  | C(33)-C(32)-C(37) | 117.78(12) |
| (C23)-H(23) | 0.9500 | (C13)-C(12)-C(11) | 117.53(11) | (C33)-C(32)-C(30) | 121.62(11) |
| (C24)-C(25) | 1.3889(16) | (C13)-C(12)-C(26) | 124.69(10) | (C37)-C(32)-C(30) | 120.54(11) |
| (C24)-H(24) | 0.9500 | (C11)-C(12)-C(26) | 117.76(11) | (C34)-C(33)-C(32) | 120.89(12) |
| (C26)-C(27) | 1.3911(18) | (C12)-C(13)-C(8) | 120.72(11) | (C34)-C(33)-H(33) | 119.6 |
| (C26)-C(31) | 1.3974(16) | (C12)-C(13)-C(1) | 128.97(10) | (C32)-C(33)-H(33) | 119.6 |
| (C27)-H(27) | 1.389(2) | (C8)-C(13)-C(1) | 110.30(10) | (C35)-C(34)-C(33) | 120.50(13) |
| (C27)-H(27) | 0.9500 | (C15)-C(14)-C(19) | 121.09(11) | (C35)-C(34)-H(34) | 119.8 |
| (C28)-C(29) | 1.387(2) | (C15)-C(14)-C(1) | 128.33(11) | C(33)-C(34)-H(34) | 119.8 |
| (C28)-H(28) | 0.9500 | (C19)-C(14)-C(1) | 110.58(10) | C(34)-C(35)-C(36) | 119.28(13) |
| (C29)-C(30) | 1.3988(18) | (C14)-C(15)-C(16) | 118.35(12) | C(34)-C(35)-H(35) | 120.4 |
| (C29)-H(29) | 0.9500 | (C14)-C(15)-H(15) | 120.8 | C(36)-C(35)-H(35) | 120.4 |
| (C30)-C(31) | 1.3987(17) | (C16)-C(15)-H(15) | 120.8 | C(35)-C(36)-C(37) | 120.46(12) |
| (C30)-C(32) | 1.4896(17) | (C17)-C(16)-C(15) | 120.55(12) | C(35)-C(36)-H(36) | 119.8 |
| (C31)-H(31) | 0.9500 | (C17)-C(16)-H(16) | 119.7 | C(37)-C(36)-H(36) | 119.8 |
| (C32)-C(33) | 1.3995(18) | (C15)-C(16)-H(16) | 119.7 | C(36)-C(37)-C(32) | 121.08(13) |
| (C32)-C(37) | 1.4005(17) | (C18)-C(17)-C(16) | 121.11(12) | C(36)-C(37)-H(37) | 119.5 |
| (C33)-C(34) | 1.3925(19) | (C18)-C(17)-H(17) | 119.4 | (C32)-C(37)-H(37) | 119.5 |
| (C33)-H(33) | 0.9500 | (C16)-C(17)-H(17) | 119.4 |

**Table S5.** Anisotropic displacement parameters (Å² x 10³) for 1-mpb-SBF. The anisotropic displacement factor exponent takes the form: \(-2\pi²[ h^2a^*2U_{11} + ... + 2h k a^* b^* U_{12} ]\)
|     | $u_{11}$ | $u_{22}$ | $u_{33}$ | $u_{23}$ | $u_{13}$ | $u_{12}$ |
|-----|----------|----------|----------|----------|----------|----------|
| C(1)| 14(1)    | 14(1)    | 13(1)    | 4(1)     | 4(1)     | 3(1)     |
| C(2)| 15(1)    | 16(1)    | 12(1)    | 3(1)     | 3(1)     | 1(1)     |
| C(3)| 18(1)    | 21(1)    | 18(1)    | 7(1)     | 6(1)     | 7(1)     |
| C(4)| 17(1)    | 27(1)    | 20(1)    | 5(1)     | 7(1)     | 5(1)     |
| C(5)| 19(1)    | 29(1)    | 17(1)    | 7(1)     | 7(1)     | 1(1)     |
| C(6)| 19(1)    | 22(1)    | 17(1)    | 9(1)     | 5(1)     | 2(1)     |
| C(7)| 14(1)    | 16(1)    | 13(1)    | 4(1)     | 2(1)     | 1(1)     |
| C(8)| 15(1)    | 14(1)    | 13(1)    | 3(1)     | 2(1)     | 1(1)     |
| C(9)| 21(1)    | 16(1)    | 20(1)    | 7(1)     | 5(1)     | 3(1)     |
| C(10)|22(1)   | 16(1)    | 24(1)    | 7(1)     | 5(1)     | 8(1)     |
| C(11)|16(1)  | 17(1)    | 21(1)    | 4(1)     | 5(1)     | 5(1)     |
| C(12)|14(1)  | 14(1)    | 13(1)    | 2(1)     | 2(1)     | 2(1)     |
| C(13)|14(1)  | 12(1)    | 12(1)    | 2(1)     | 1(1)     | 1(1)     |
| C(14)|14(1)  | 14(1)    | 18(1)    | 4(1)     | 7(1)     | 4(1)     |
| C(15)|17(1)  | 21(1)    | 18(1)    | 3(1)     | 5(1)     | 4(1)     |
| C(16)|20(1)  | 20(1)    | 28(1)    | -3(1)    | 7(1)     | 0(1)     |
| C(17)|25(1)  | 15(1)    | 40(1)    | 5(1)     | 15(1)    | 1(1)     |
| C(18)|24(1)  | 18(1)    | 30(1)    | 11(1)    | 14(1)    | 6(1)     |
| C(19)|15(1)  | 16(1)    | 19(1)    | 7(1)     | 8(1)     | 6(1)     |
| C(20)|16(1)  | 18(1)    | 17(1)    | 7(1)     | 7(1)     | 7(1)     |
| C(21)|24(1)  | 27(1)    | 20(1)    | 13(1)    | 8(1)     | 9(1)     |
| C(22)|24(1)  | 37(1)    | 14(1)    | 8(1)     | 4(1)     | 9(1)     |
| C(23)|19(1)  | 28(1)    | 17(1)    | 1(1)     | 4(1)     | 2(1)     |
| C(24)|18(1)  | 18(1)    | 19(1)    | 4(1)     | 6(1)     | 3(1)     |
| C(25)|13(1)  | 18(1)    | 14(1)    | 6(1)     | 5(1)     | 6(1)     |
| C(26)|16(1)  | 17(1)    | 18(1)    | 7(1)     | 6(1)     | 7(1)     |
| C(27)|31(1)  | 21(1)    | 19(1)    | 5(1)     | 5(1)     | 1(1)     |
| C(28)|48(1)  | 28(1)    | 16(1)    | 7(1)     | 9(1)     | 2(1)     |
| C(29)|37(1)  | 25(1)    | 21(1)    | 11(1)    | 13(1)    | 4(1)     |
| C(30)|19(1)  | 17(1)    | 20(1)    | 7(1)     | 8(1)     | 7(1)     |
| C(31)|15(1)  | 19(1)    | 16(1)    | 5(1)     | 6(1)     | 6(1)     |
| C(32)|18(1)  | 19(1)    | 21(1)    | 11(1)    | 9(1)     | 7(1)     |
| C(33)|21(1)  | 26(1)    | 26(1)    | 6(1)     | 13(1)    | 1(1)     |
| C(34)|28(1)  | 29(1)    | 24(1)    | 4(1)     | 11(1)    | -1(1)    |
Table S6. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\AA^2 \times 10^3$) for 1-mtp-SBF. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

|     | x     | y     | z     | U(eq) | x     |
|-----|-------|-------|-------|-------|-------|
| C(1)| 6134(1)| 3587(1)| 1921(1)| 21(1) | C(1)  |
| C(2)| 5386(1)| 4153(1)| 2165(1)| 21(1) | C(2)  |
| C(3)| 5513(1)| 4927(1)| 2783(1)| 22(1) | C(3)  |
| C(4)| 4707(1)| 5319(1)| 2885(1)| 28(1) | C(4)  |
| C(5)| 3819(1)| 4933(1)| 2415(1)| 29(1) | C(5)  |
| C(6)| 3697(1)| 4157(1)| 1811(1)| 26(1) | C(6)  |
| C(7)| 4484(1)| 3782(1)| 1667(1)| 22(1) | C(7)  |
| C(8)| 4560(1)| 3029(1)| 1011(1)| 22(1) | C(8)  |
| C(9)| 3874(1)| 2486(1)| 326(1) | 26(1) | C(9)  |
| C(10)| 4144(1)| 1858(1)| -247(1)| 29(1) | C(10) |
| C(11)| 5089(1)| 1770(1)| -143(1)| 30(1) | C(11) |
| C(12)| 5781(1)| 2304(1)| 548(1) | 26(1) | C(12) |
| C(13)| 5512(1)| 2930(1)| 1123(1)| 22(1) | C(13) |
| C(14)| 6805(1)| 3063(1)| 2819(1)| 22(1) | C(14) |
| C(15)| 6591(1)| 2418(1)| 3415(1)| 28(1) | C(15) |
| C(16)| 7320(1)| 2063(1)| 4226(1)| 34(1) | C(16) |
| C(17)| 8244(1)| 2365(1)| 4446(1)| 34(1) | C(17) |
| C(18)| 8460(1)| 3002(1)| 3845(1)| 29(1) | C(18) |
| C(19)| 7740(1)| 3340(1)| 3018(1)| 23(1) | C(19) |
| C(20)| 7755(1)| 4003(1)| 2255(1)| 24(1) | C(20) |
| C(21)| 8505(1)| 4446(1)| 2102(1)| 33(1) | C(21) |
| C(22)| 8316(1)| 5059(1)| 1328(1)| 39(1) | C(22) |
| C(23)| 7395(1)| 5232(1)| 699(1) | 35(1) | C(23) |
| C(24)| 6641(1)| 4785(1)| 840(1) | 28(1) | C(24) |
| C(25)| 6827(1)| 4168(1)| 1619(1)| 22(1) | C(25) |
| C(26)| 6469(1)| 5299(1)| 3377(1)| 22(1) | C(26) |
Table S7. Bond lengths [Å] and angles [°] for **1-mtp-SBF**.

| Bond                        | Length  | Angle     |
|-----------------------------|---------|-----------|
| C(1)-C(25)                  | 1.5249(18) | C(39)-H(39) | 0.9500 | C(22)-C(21)-C(20) | 118.81(14) |
| C(1)-C(13)                  | 1.5292(18) | C(40)-C(41) | 1.382(2) | C(22)-C(21)-H(21) | 120.6 |
| C(1)-C(14)                  | 1.5340(18) | C(40)-H(40) | 0.9500 | C(20)-C(21)-H(21) | 120.6 |
| C(1)-C(2)                   | 1.5364(18) | C(41)-C(42) | 1.381(2) | C(21)-C(22)-C(23) | 120.74(14) |
| C(2)-C(3)                   | 1.3958(18) | C(41)-H(41) | 0.9500 | C(21)-C(22)-H(22) | 119.6 |
| C(2)-C(7)                   | 1.4029(18) | C(42)-C(43) | 1.388(2) | C(23)-C(22)-H(22) | 119.6 |
| C(3)-C(4)                   | 1.4009(19) | C(42)-H(42) | 0.9500 | C(22)-C(23)-C(24) | 120.88(14) |
| C(3)-C(26)                  | 1.4956(18) | C(43)-H(43) | 0.9500 | C(22)-C(23)-H(23) | 119.6 |
| C(4)-C(5)                   | 1.388(2) | C(25)-C(1)-C(13) | 114.60(10) | C(24)-C(23)-H(23) | 119.6 |
| C(4)-H(4)                   | 0.9500 | C(25)-C(1)-C(13) | 101.36(10) | C(25)-C(24)-H(23) | 118.57(14) |
| Bond                                | Distance | Angle 1     | Angle 2     | Angle 3     |
|-------------------------------------|----------|-------------|-------------|-------------|
| C(5)-C(6)                           | 1.387(2) | 112.78(11)  | C(23)       | 120.7       |
| C(5)-H(5)                           | 0.9500   | C(25)-C(1)- | C(24)-C(24)- | 120.7       |
| C(6)-C(7)                           | 1.3923(19)| 115.05(11)  | C(24)-C(25)- | 120.65(12)  |
| C(6)-H(6)                           | 0.9500   | C(13)-C(1)- | C(13)-C(1)- | 128.74(12)  |
| C(7)-H(7)                           | 0.9500   | C(14)-C(1)- | H(24)       | 110.60(11)  |
| C(7)-C(8)                           | 1.4717(18)| 112.36(10)  | C(25)-C(25)- | 119.09(12)  |
| C(8)-C(9)                           | 1.3916(18)| 1.4021(18)  | C(25)-C(25)- | 117.86(12)  |
| C(8)-C(13)                          | 1.386(2) | 1.392(2)    | C(25)-C(25)- | 123.04(12)  |
| C(9)-C(10)                          | 0.9500   | 1.3916(18)  | C(25)-C(25)- | 121.65(12)  |
| C(9)-H(9)                           | 0.9500   | 1.4021(18)  | C(25)-C(25)- | 119.2       |
| C(10)-C(11)                         | 0.9500   | 1.392(2)    | C(25)-C(25)- | 119.2       |
| C(10)-H(10)                         | 0.9500   | 1.3916(18)  | C(25)-C(25)- | 118.42(12)  |
| C(11)-C(12)                         | 1.393(2) | 1.392(2)    | C(25)-C(25)- | 122.55(12)  |
| C(11)-H(11)                         | 0.9500   | 1.3916(18)  | C(25)-C(25)- | 119.01(11)  |
| C(12)-C(13)                         | 1.3842(19)| 1.3815(19)  | C(25)-C(25)- | 119.4       |
| C(12)-H(12)                         | 0.9500   | 1.3996(19)  | C(25)-C(25)- | 119.4       |
| C(14)-C(15)                         | 1.394(2) | 1.394(2)    | C(25)-C(25)- | 118.85(12)  |
| C(14)-H(15)                         | 0.9500   | 1.394(2)    | C(25)-C(25)- | 121.26(12)  |
| C(16)-C(17)                         | 1.391(2) | 1.391(2)    | C(25)-C(25)- | 119.88(12)  |
| C(16)-H(16)                         | 0.9500   | 1.391(2)    | C(25)-C(25)- | 120.72(12)  |
| C(17)-C(18)                         | 1.383(2) | 1.383(2)    | C(25)-C(25)- | 119.6       |
| C(18) | 0.9500 | C(8) | C(9)-C(8)-C(13) | 120.07(12) | H(31) | C(30)-C(31)-H(31) | 119.6 |
|---|---|---|---|---|---|---|---|
| C(17) | 1.3906(19) | C(9) | C(9)-C(8)-C(7) | 131.33(12) | C(37)-C(32)-C(33) | 118.13(12) |
| C(19) | 0.9500 | C(13)-C(8)-C(7) | 108.53(11) | C(37)-C(32)-C(28) | 122.18(12) |
| C(18) | 1.4677(19) | C(10)-C(9)-C(8) | 119.08(13) | C(33)-C(32)-C(28) | 119.66(12) |
| H(18) | C(9) | C(8)-C(7) | 131.33(12) | C(37)-C(32)-C(28) | 119.66(12) |
| C(19) | 1.3892(19) | C(10)-C(9)-H(9) | 120.5 | C(34)-C(33)-C(32) | 121.28(13) |
| C(20) | 1.4002(19) | C(8)-C(9)-H(9) | 120.5 | C(34)-C(33)-H(33) | 119.4 |
| C(21) | 1.384(2) | C(9)-C(10)-C(11) | 120.68(13) | C(32)-C(33)-H(33) | 119.4 |
| C(20) | 0.9500 | C(9)-C(10)-H(10) | 119.7 | C(33)-C(34)-C(35) | 119.83(13) |
| C(21) | 1.386(2) | C(11)-C(10)-H(10) | 119.7 | C(33)-C(34)-H(34) | 120.1 |
| C(22) | 0.9500 | C(10)-C(11)-C(12) | 120.58(13) | C(35)-C(34)-H(34) | 120.1 |
| H(22) | C(23) | 1.390(2) | C(10)-C(11)-H(11) | 119.7 | C(36)-C(35)-C(34) | 119.77(14) |
| C(23) | 0.9500 | C(12)-C(11)-H(11) | 119.7 | C(36)-C(35)-H(35) | 120.1 |
| H(23) | C(24) | 1.3839(19) | C(13)-C(12)-C(11) | 118.82(13) | C(34)-C(35)-H(35) | 120.1 |
| C(24) | 0.9500 | C(13)-C(12)-H(12) | 120.6 | C(35)-C(36)-C(37) | 120.16(14) |
| H(24) | C(26) | 1.3879(18) | C(11)-C(12)-H(12) | 120.6 | C(35)-C(36)-H(36) | 119.9 |
| C(27) | 1.3946(18) | C(12)-C(13)-C(8) | 120.75(13) | C(37)-C(36)-H(36) | 119.9 |
| C(31) | C(27) | 1.3943(18) | C(12)-C(13)-C(1) | 128.52(12) | C(36)-C(37)-C(32) | 120.79(13) |
| C(28) | 0.9500 | C(8)-C(13)-C(1) | 110.73(11) | C(36)-C(37)-H(37) | 119.6 |
| C(27) | C(29) | 1.3929(18) | C(15)-C(14)-C(19) | 120.67(13) | C(32)-C(37)-H(37) | 119.6 |
| C(28) | 1.4835(18) | C(15)-C(14)-C(1) | 128.77(12) | C(43)-C(38)-C(39) | 118.18(13) |
| C(32) | C(29) | 1.4005(18) | C(19)-C(14)-C(1) | 110.54(11) | C(43)-C(38)-C(30) | 121.09(13) |
| C(30) | C(29) | 0.9500 | C(14)-C(15)-H(18) | 118.75(14) | C(39)-C(38)-H(38) | 120.73(13) |
| Atom     | Atom     | Distance (Å) | Angle (°)   | atom     | Distance (Å) | Angle (°)   |
|----------|----------|--------------|-------------|----------|--------------|-------------|
| C(30)    | C(16)    | 1.3974(19)   | 120.6       | C(30)    | C(16)        | 120.6       |
| C(30)    | C(15)    | 1.3974(19)   | 120.6       | C(30)    | C(15)        | 120.6       |
| C(30)    | H(15)    | 1.3974(19)   | 120.6       | C(30)    | C(15)        | 120.6       |
| C(30)    | C(15)    | 1.3974(19)   | 120.6       | C(30)    | C(15)        | 120.6       |
| C(30)    | C(15)    | 1.3974(19)   | 120.6       | C(30)    | C(15)        | 120.6       |
| C(30)    | C(15)    | 1.3974(19)   | 120.6       | C(30)    | C(15)        | 120.6       |
| C(30)    | C(15)    | 1.3974(19)   | 120.6       | C(30)    | C(15)        | 120.6       |
| C(30)    | C(15)    | 1.3974(19)   | 120.6       | C(30)    | C(15)        | 120.6       |
| C(30)    | C(15)    | 1.3974(19)   | 120.6       | C(30)    | C(15)        | 120.6       |
| C(30)    | C(15)    | 1.3974(19)   | 120.6       | C(30)    | C(15)        | 120.6       |
| C(30)    | C(15)    | 1.3974(19)   | 120.6       | C(30)    | C(15)        | 120.6       |
| C(30)    | C(15)    | 1.3974(19)   | 120.6       | C(30)    | C(15)        | 120.6       |
| C(30)    | C(15)    | 1.3974(19)   | 120.6       | C(30)    | C(15)        | 120.6       |
| C(30)    | C(15)    | 1.3974(19)   | 120.6       | C(30)    | C(15)        | 120.6       |
| C(30)    | C(15)    | 1.3974(19)   | 120.6       | C(30)    | C(15)        | 120.6       |
| C(30)    | C(15)    | 1.3974(19)   | 120.6       | C(30)    | C(15)        | 120.6       |
| C(30)    | C(15)    | 1.3974(19)   | 120.6       | C(30)    | C(15)        | 120.6       |
| C(30)    | C(15)    | 1.3974(19)   | 120.6       | C(30)    | C(15)        | 120.6       |
| C(30)    | C(15)    | 1.3974(19)   | 120.6       | C(30)    | C(15)        | 120.6       |
| C(30)    | C(15)    | 1.3974(19)   | 120.6       | C(30)    | C(15)        | 120.6       |
| C(30)    | C(15)    | 1.3974(19)   | 120.6       | C(30)    | C(15)        | 120.6       |
| C(30)    | C(15)    | 1.3974(19)   | 120.6       | C(30)    | C(15)        | 120.6       |
| C(30)    | C(15)    | 1.3974(19)   | 120.6       | C(30)    | C(15)        | 120.6       |
| C(30)    | C(15)    | 1.3974(19)   | 120.6       | C(30)    | C(15)        | 120.6       |
| C(30)    | C(15)    | 1.3974(19)   | 120.6       | C(30)    | C(15)        | 120.6       |
| C(30)    | C(15)    | 1.3974(19)   | 120.6       | C(30)    | C(15)        | 120.6       |
| C(30)    | C(15)    | 1.3974(19)   | 120.6       | C(30)    | C(15)        | 120.6       |
| C(30)    | C(15)    | 1.3974(19)   | 120.6       | C(30)    | C(15)        | 120.6       |
| C(30)    | C(15)    | 1.3974(19)   | 120.6       | C(30)    | C(15)        | 120.6       |

**Table S8.** Anisotropic displacement parameters (Å\(^2\) × 10\(^3\)) for 1-mtp-SBF. The anisotropic displacement factor exponent takes the form: \(-2\pi^2 [h^2 a^* a_{11} + ... + 2h k a^* b^* U_{12}]\).
| C(1) | 21(1) | 21(1) | 23(1) | -1(1) | 9(1) | 0(1) |
| C(2) | 21(1) | 22(1) | 21(1) | 3(1)  | 8(1) | 1(1) |
| C(3) | 23(1) | 22(1) | 20(1) | 3(1)  | 7(1) | 1(1) |
| C(4) | 30(1) | 27(1) | 27(1) | -3(1) | 11(1)| 4(1) |
| C(5) | 24(1) | 35(1) | 29(1) | 0(1)  | 11(1)| 6(1) |
| C(6) | 20(1) | 33(1) | 24(1) | 1(1)  | 7(1) | -1(1)|
| C(7) | 21(1) | 24(1) | 21(1) | 2(1)  | 7(1) | -1(1)|
| C(8) | 23(1) | 22(1) | 21(1) | 2(1)  | 8(1) | 0(1) |
| C(9) | 21(1) | 29(1) | 26(1) | 1(1)  | 7(1) | -3(1)|
| C(10)| 30(1) | 28(1) | 27(1) | -4(1) | 6(1) | -6(1)|
| C(11)| 34(1) | 28(1) | 27(1) | -7(1) | 11(1)| -1(1)|
| C(12)| 26(1) | 27(1) | 28(1) | -1(1) | 12(1)| 1(1) |
| C(13)| 22(1) | 21(1) | 22(1) | 2(1)  | 7(1) | -2(1)|
| C(14)| 24(1) | 20(1) | 21(1) | -4(1) | 9(1) | 2(1) |
| C(15)| 34(1) | 24(1) | 30(1) | -2(1) | 16(1)| 0(1) |
| C(16)| 49(1) | 27(1) | 29(1) | 4(1)  | 17(1)| 7(1) |
| C(17)| 42(1) | 34(1) | 23(1) | -1(1) | 6(1) | 14(1)|
| C(18)| 26(1) | 30(1) | 26(1) | -7(1) | 4(1) | 5(1) |
| C(19)| 23(1) | 22(1) | 24(1) | -6(1) | 8(1) | 2(1) |
| C(20)| 22(1) | 25(1) | 25(1) | -5(1) | 9(1) | -1(1)|
| C(21)| 24(1) | 39(1) | 35(1) | -2(1) | 10(1)| -7(1)|
| C(22)| 37(1) | 43(1) | 42(1) | -2(1) | 20(1)| -15(1)|
| C(23)| 45(1) | 33(1) | 29(1) | 0(1)  | 16(1)| -9(1)|
| C(24)| 29(1) | 28(1) | 26(1) | 0(1)  | 9(1) | -1(1)|
| C(25)| 23(1) | 22(1) | 23(1) | -4(1) | 10(1)| -1(1)|
| C(26)| 23(1) | 21(1) | 22(1) | -4(1) | 9(1) | 2(1) |
| C(27)| 26(1) | 20(1) | 23(1) | -2(1) | 11(1)| -1(1)|
| C(28)| 22(1) | 20(1) | 20(1) | -2(1) | 9(1) | 2(1) |
| C(29)| 21(1) | 23(1) | 24(1) | -3(1) | 9(1) | 0(1) |
| C(30)| 24(1) | 20(1) | 24(1) | -1(1) | 12(1)| 1(1) |
| C(31)| 26(1) | 22(1) | 22(1) | 1(1)  | 9(1) | 4(1) |
| C(32)| 26(1) | 18(1) | 21(1) | -5(1) | 8(1) | -2(1)|
| C(33)| 25(1) | 25(1) | 28(1) | -1(1) | 9(1) | -3(1)|
| C(34)| 35(1) | 29(1) | 31(1) | 7(1)  | 12(1)| -3(1)|
| C(35)| 40(1) | 29(1) | 30(1) | 8(1)  | 6(1) | 4(1) |
| C(36)| 26(1) | 31(1) | 32(1) | -2(1) | 5(1) | 5(1) |
4 Molecular Modeling

**Figure S1.** Representation of the energy levels and the main molecular orbitals involved in the electronic transitions of 1-p-SBF obtained by TD-DFT m06-2x and the 6-311+G(d, p) basis set on the geometry of $S_0$, shown with an isovalues of 0.04 [e bohr$^{-3}$]$^{1/2}$ (for clarity purpose, only the main contribution for each transition is shown, see details in Table below).
**Figure S2.** Representation of the energy levels and the main molecular orbitals involved in the electronic transitions of 1-**mbp-SBF** obtained by TD-DFT m06-2x and the 6-311+G(d, p) basis set on the geometry of $S_0$, shown with an isovales of 0.04 [e bohr$^{-3}$]$^{1/2}$ (for clarity purpose, only the main contribution for each transition is shown, see details in Table below).

**Figure S3.** Representation of the energy levels and the main molecular orbitals involved in the electronic transitions of 1-**mtp-SBF** obtained by TD-DFT m06-2x and the 6-311+G(d, p) basis set on the geometry of $S_0$, shown with an isovales of 0.04 [e bohr$^{-3}$]$^{1/2}$ (for clarity purpose, only the main contribution for each transition is shown, see details in Table below).
**Figure S4.** Representation of the energy levels and the main molecular orbitals involved in the electronic transitions of 1-mqp-SBF obtained by TD-DFT m06-2x and the 6-311+G(d, p) basis set on the geometry of S0, shown with an isovalue of 0.04 [e \cdot \text{bohr}^{-3}]^{1/2} (for clarity purpose, only the main contribution for each transition is shown, see details in Table below).

**Figure S5.** Natural transition orbital pairs (“hole” on the top and “electron” on the bottom) for the four first singlet excited states obtained by TD-DFT (M06-2X, 6-311+g(d, p), isovalue of 0.04) of 1-p-SBF.
Figure S6. Natural transition orbital pairs (“hole” on the top and “electron” on the bottom) for the four first singlet excited states obtained by TD-DFT (M06-2X, 6-311+g(d, p), isovalue of 0.04) of 1-mpb-SBF.

Figure S7. Natural transition orbital pairs (“hole” on the top and “electron” on the bottom) for the four first singlet excited states obtained by TD-DFT (M06-2X, 6-311+g(d, p), isovalue of 0.04) of 1-mtp-SBF.
Figure S8. Natural transition orbital pairs (“hole” on the top and “electron” on the bottom) for the four first singlet excited states obtained by TD-DFT (M06-2X, 6-311+g(d, p), isovalue of 0.04) of 1-mqp-SBF.

Table S9. Results of TD-DFT calculations for 1-p-SBF (m06-2x/6-311+g(d, p)).

| λ (nm) | Osc. strength | Major contribs | Minor contribs |
|--------|---------------|----------------|----------------|
| 268    | 0.184         | HOMO→LUMO (59%) | H-2→LUMO (2%), H-1→LUMO (5%), H-1→L+1 (6%), H-1→L+2 (5%), HOMO→L+1 (7%), HOMO→L+3 (2%) |
| 267    | 0.182         | HOMO→L+1 (60%)  | H-3→L+1 (2%), H-1→LUMO (8%), H-1→L+1 (3%), H-1→L+3 (6%), HOMO→LUMO (5%), HOMO→L+2 (3%) |
| 258    | 0.075         | H-1→LUMO (10%), H-1→L+3 (15%), HOMO→L+2 (38%) | H-7→LUMO (2%), H-2→LUMO (2%), H-1→L+2 (7%), HOMO→LUMO (4%), HOMO→L+1 (3%), HOMO→L+3 (9%) |
| 257    | 0.064         | H-1→L+2 (14%), HOMO→L+2 (14%), HOMO→L+3 (39%) | H-3→L+1 (3%), H-1→L+1 (7%), H-1→L+3 (3%), HOMO→LUMO (2%), HOMO→L+1 (6%) |
| 243    | 0.004         | H-4→L+1 (17%), H-2→L+1 (14%), HOMO→L+8 (10%) | H-6→L+1 (6%), H-4→LUMO (3%), H-3→L+1 (8%), H-1→L+8 (5%), HOMO→L+12 (2%), HOMO→L+15 (4%) |
| 243    | 0.009         | H-4→LUMO (21%), H-2→LUMO (10%) | H-6→LUMO (7%), H-4→L+1 (3%), H-3→LUMO (6%), H-1→L+7 (3%), H-1→L+8 (7%), H-1→L+15 (3%), HOMO→L+7 (4%), HOMO→L+8 (5%), HOMO→L+15 (4%) |
| 234    | 0.111         | H-1→LUMO (65%), H-2→LUMO (2%), HOMO→L+1 (3%), |

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|    |        |                          |                          |
|----|--------|--------------------------|--------------------------|
|    |        | HOMO→LUMO                | HOMO→L+2 (7%), HOMO→L+3 (5%) |
| 231| 0.012  | H-5→L+9 (10%)            | H-6→LUMO (2%), H-6→L+12 (3%), H-5→LUMO (3%), H-5→L+2 (7%), H-5→L+7 (6%), H-2→LUMO (2%), H-2→L+2 (9%), H-2→L+8 (5%), H-2→L+12 (7%), H-1→L+1 (6%), H-1→L+2 (4%), HOMO→LUMO (3%) |
| 230| 0.093  | H-1→L+1 (63%)            | H-3→L+1 (2%), H-2→L+1 (3%), H-1→LUMO (3%), HOMO→L+1 (7%), HOMO→L+2 (3%), HOMO→L+3 (8%) |
| 225| 0.123  | H-1→L+2 (17%), H-1→L+3 (23%), HOMO→L+2 (16%), HOMO→L+3 (12%) | H-2→LUMO (3%), H-2→L+3 (2%), HOMO→LUMO (4%) |
| 223| 0.077  | H-1→L+2 (26%), H-1→L+3 (20%), HOMO→L+2 (11%), HOMO→L+3 (13%) | H-1→L+1 (4%), HOMO→L+1 (8%) |
| 221| 0.030  | H-2→LUMO (42%), H-2→L+2 (16%) | H-4→L+3 (2%), H-3→LUMO (4%), HOMO→LUMO (6%), HOMO→L+3 (3%) |
| 217| 0.0007 | H-1→L+5 (13%), HOMO→L+4 (68%) | H-4→LUMO (3%), H-3→L+1 (7%), H-2→LUMO (3%), H-2→L+2 (5%), HOMO→L+8 (9%) |
| 215| 0.098  | H-2→L+1 (44%), H-1→L+3 (10%) | H-7→L+1 (3%), H-4→L+3 (2%), H-3→L+2 (2%), H-2→LUMO (6%), H-2→L+1 (3%), H-2→L+3 (2%), H-1→L+2 (9%), HOMO→L+8 (3%) |
| 214| 0.086  | H-3→LUMO (15%), H-3→L+1 (12%), H-2→L+2 (20%) | H-7→L+1 (3%), H-4→L+3 (2%), H-3→L+2 (2%), H-2→LUMO (6%), H-2→L+1 (3%), H-2→L+3 (2%), H-1→L+2 (9%), HOMO→L+8 (3%) |
| 213| 0.004  | H-1→L+4 (39%), HOMO→L+5 (34%) | H-1→L+5 (4%), HOMO→L+4 (4%), HOMO→L+7 (4%) |
| 212| 0.015  | H-4→LUMO (14%), H-3→LUMO (37%), H-3→L+1 (16%) | H-7→LUMO (3%), H-2→LUMO (5%), H-1→L+3 (8%) |
| 210| 0.209  | H-4→L+1 (13%), H-4→L+3 (14%), H-2→L+1 (12%), HOMO→L+8 (12%) | H-5→LUMO (2%), H-4→LUMO (8%), H-3→LUMO (2%), H-3→L+1 (4%), H-3→L+8 (2%), H-2→LUMO (3%), H-2→L+3 (3%), HOMO→L+7 (4%) |
| 210| 0.244  | H-3→L+1 (20%), HOMO→L+8 (11%) | H-5→L+2 (2%), H-4→LUMO (4%), H-4→L+1 (9%), H-2→LUMO (2%), H-2→L+1 (9%), H-2→L+2 (9%), H-2→L+3 (8%), H-1→L+3 (2%), H-1→L+7 (4%) |
Table S10. Results of TD-DFT calculations for 1-mbp-SBF (m06-2x/6-311+g(d, p)).

| $\lambda$ (nm) | Osc. strength | Major contribs | Minor contribs |
|----------------|---------------|----------------|----------------|
| 207            | 0.022         | H-2→L+3 (41%)  | H-6→L+3 (2%), H-5→L+1 (3%), H-4→L+1 (9%), H-4→L+2 (4%), H-3→L+2 (4%), H-3→L+3 (2%), H-2→L+2 (5%), H-1→L+8 (2%), HOMO→L+8 (4%) |
| 269            | 0.158         | HOMO→LUMO (33%), HOMO→L+1 (34%) | H-2→L+1 (3%), H-2→L+3 (2%), H-1→LUMO (3%), H-1→L+1 (5%), H-1→L+3 (3%), HOMO→L+2 (3%) |
| 268            | 0.210         | HOMO→LUMO (26%), HOMO→L+1 (36%) | H-2→LUMO (3%), H-1→LUMO (9%), H-1→L+4 (4%), HOMO→L+3 (2%) |
| 257            | 0.085         | H-1→L+4 (15%), HOMO→L+3 (27%), HOMO→L+4 (15%) | H-4→LUMO (3%), H-2→L+4 (4%), H-1→LUMO (9%), H-1→L+3 (6%), HOMO→LUMO (3%) |
| 257            | 0.038         | HOMO→L+3 (25%), HOMO→L+4 (30%) | H-4→L+1 (4%), H-2→L+1 (3%), H-2→L+3 (5%), H-1→L+1 (4%), H-1→L+3 (9%), HOMO→L+1 (7%) |
| 244            | 0.099         | H-7→L+1 (4%), H-7→L+2 (3%), H-5→L+1 (6%), H-4→L+1 (3%), H-3→LUMO (6%), H-3→L+1 (8%), H-2→LUMO (3%), H-2→L+2 (2%), H-2→L+3 (2%), H-2→L+12 (3%), H-1→LUMO (6%), H-1→L+2 (6%), H-1→L+8 (6%), HOMO→L+2 (3%), HOMO→L+18 (5%) |
| 244            | 0.033         | H-5→LUMO (14%) | H-7→L+1 (3%), H-7→L+2 (4%), H-3→LUMO (6%), H-3→L+1 (6%), H-3→L+2 (5%), H-2→L+3 (3%), H-2→L+8 (2%), H-1→L+3 (3%), H-1→L+8 (6%), HOMO→L+2 (3%), HOMO→L+10 (3%), HOMO→L+12 (4%) |
| Page | Value | Transition 1 | Transition 2 | Transition 3 | Transition 4 |
|------|-------|-------------|-------------|-------------|-------------|
| 242  | 0.331 | H-2→L+2 (21%), H-1→LUMO (19%), H-1→L+2 (14%) | H-7→L+1 (3%), H-5→L+1 (4%), H-4→L+1 (2%), H-3→L+1 (5%), H-2→LUMO (4%), HOMO→LUMO (6%) |
| 241  | 0.003 | H-5→LUMO (18%) | H-7→LUMO (9%), H-5→L+1 (3%), H-5→L+2 (2%), H-3→L+2 (7%), H-2→L+3 (4%), H-2→L+8 (8%), H-1→L+12 (5%), H-1→L+18 (3%), HOMO→L+8 (5%), HOMO→L+18 (4%) |
| 237  | 0.0002 | H-6→L+2 (29%), H-2→L+9 (10%), H-2→L+10 (10%) | H-6→LUMO (7%), H-6→L+23 (2%), H-2→L+8 (2%), H-1→L+9 (7%), H-1→L+10 (7%) |
| 234  | 0.065 | H-2→LUMO (26%), H-1→LUMO (29%), H-1→L+2 (12%), HOMO→LUMO (12%) | H-2→L+2 (3%), HOMO→L+1 (3%), HOMO→L+3 (5%), HOMO→L+4 (3%) |
| 231  | 0.113 | H-2→L+1 (11%), H-1→L+1 (63%) | H-4→L+1 (2%), HOMO→L+1 (5%), HOMO→L+3 (4%), HOMO→L+4 (5%) |
| 224  | 0.116 | H-1→L+4 (13%), HOMO→L+3 (10%), HOMO→L+4 (26%) | H-4→LUMO (3%), H-4→L+4 (2%), H-2→L+3 (5%), H-2→L+4 (3%), H-1→L+3 (8%), HOMO→LUMO (9%), HOMO→L+2 (6%) |
| 223  | 0.111 | H-1→L+1 (10%), H-1→L+4 (16%), HOMO→L+3 (17%) | H-4→L+1 (3%), H-2→L+1 (7%), H-2→L+3 (7%), H-2→L+4 (4%), H-1→L+3 (8%), HOMO→L+1 (4%), HOMO→L+2 (3%), HOMO→L+4 (5%) |
| 222  | 0.019 | H-2→LUMO (10%), H-2→L+1 (12%), H-1→L+3 (25%), HOMO→L+2 (18%) | H-3→LUMO (9%), H-1→LUMO (3%), HOMO→L+1 (2%) |
| 220  | 0.014 | H-2→L+1 (47%), H-1→L+1 (11%) | H-4→L+1 (3%), H-3→LUMO (6%), H-1→L+4 (5%), HOMO→L+2 (9%) |
| 217  | 0.039 | H-3→LUMO (17%), HOMO→L+2 (24%), HOMO→L+5 (22%) | H-2→LUMO (5%), H-2→L+2 (5%), H-1→L+7 (3%), HOMO→L+6 (2%) |
| 216  | 0.053 | HOMO→L+2 (13%), HOMO→L+5 (36%) | H-3→LUMO (7%), H-2→LUMO (2%), H-2→L+2 (3%), H-1→L+7 (2%) |
| λ (nm) | Osc. strength | Major contribs | Minor contribs |
|--------|---------------|----------------|----------------|
| 269    | 0.125         | HOMO→LUMO (12%), HOMO→L+1 (56%) | H-4→L+1 (2%), H-2→L+1 (4%), H-1→LUMO (2%), HOMO→L+2 (3%), HOMO→L+3 (3%) |
| 268    | 0.218         | H-1→LUMO (15%), HOMO→LUMO (32%), HOMO→L+1 (17%) | H-4→LUMO (2%), H-2→LUMO (2%), H-2→L+2 (3%), H-1→L+2 (5%), HOMO→L+2 (9%) |
| 258    | 0.033         | HOMO→L+3 (17%), HOMO→L+4 (22%) | H-4→L+1 (2%), H-3→LUMO (7%), H-3→L+2 (5%), H-2→L+1 (3%), H-2→L+4 (3%), H-1→L+2 (2%), H-1→L+3 (8%), HOMO→L+1 (6%), HOMO→L+6 (4%) |
| 258    | 0.086         | H-1→LUMO (13%), H-1→L+5 (14%), HOMO→L+5 (19%) | H-4→LUMO (4%), H-2→L+4 (4%), H-2→L+5 (5%), H-1→L+3 (2%), H-1→L+4 (6%), HOMO→LUMO (2%), HOMO→L+3 (6%), HOMO→L+6 (5%) |
| 255    | 0.008         | H-3→LUMO (11%), H-2→L+3 (14%), H-1→L+3 (10%), H-3→L+2 (9%), H-1→L+6 (3%), HOMO→L+1 (2%), HOMO→L+6 (5%) |

Table S11. Results of TD-DFT calculations for 1-mtp-SBF (m06-2x/6-311+g(d, p)).
| Energy (eV) | Charge Transfer | Notes |
|------------|-----------------|-------|
| 250        | H-1→LUMO (28%), H-1→L+2 (11%), HOMO→LUMO (21%), HOMO→L+2 (12%) | H-3→L+3 (4%), H-2→LUMO (4%), H-2→L+2 (7%) |
| 243        | H-5→L+1 (35%) | H-6→L+1 (2%), H-4→L+1 (4%), H-3→L+1 (6%), H-2→L+20 (2%), HOMO→L+11 (2%), HOMO→L+12 (4%), HOMO→L+13 (7%), HOMO→L+20 (5%) |
| 242        | H-6→LUMO (34%) | H-13→L+5 (2%), H-6→L+2 (7%), H-5→LUMO (2%), H-2→L+13 (3%), H-1→L+12 (3%), H-1→L+13 (6%), H-1→L+20 (4%), HOMO→L+13 (3%), HOMO→L+20 (4%) |
| 239        | H-3→LUMO (23%), H-3→L+2 (20%), H-1→L+3 (11%) | H-8→L+2 (2%), H-3→L+9 (2%), H-2→L+3 (6%), H-1→L+6 (2%), HOMO→L+3 (6%) |
| 238        | H-8→L+2 (12%), H-3→L+11 (11%) | H-8→LUMO (4%), H-8→L+3 (2%), H-8→L+6 (2%), H-7→LUMO (2%), H-7→L+3 (4%), H-2→L+9 (5%), H-2→L+10 (4%), H-1→L+1 (2%), H-1→L+9 (8%), H-1→L+10 (5%) |
| 237        | H-7→L+3 (11%), H-1→L+11 (11%) | H-8→L+3 (3%), H-7→LUMO (7%), H-7→L+2 (5%), H-3→LUMO (2%), H-3→L+9 (6%), H-3→L+10 (5%), H-2→L+11 (8%), HOMO→L+11 (2%) |
| 236        | H-2→LUMO (40%), H-1→L+2 (15%), HOMO→LUMO (19%) | H-3→L+3 (3%), H-1→LUMO (7%), HOMO→L+5 (2%) |
| 230        | H-2→L+1 (11%), H-1→L+1 (67%) | H-4→L+1 (3%), HOMO→L+4 (3%) |
| 227        | H-1→LUMO (10%), HOMO→L+2 (51%) | H-2→L+2 (5%), HOMO→LUMO (3%), HOMO→L+3 (4%), HOMO→L+4 (3%), HOMO→L+5 (7%) |
| 225        | HOMO→L+4 (13%), HOMO→L+5 (18%) | H-4→LUMO (2%), H-4→L+5 (2%), H-2→L+2 (2%), H-2→L+3 (5%) |
| λ  (nm) | Osc. strength | Major contribs | Minor contribs |
|--------|---------------|----------------|----------------|
| 269    | 0.125         | HOMO→LUMO (19%), HOMO→L+1 (26%), HOMO→L+2 (14%), HOMO→L+3 (10%) | H-3→L+2 (2%), H-3→L+4 (2%), H-1→LUMO (4%), H-1→L+1 (2%), H-1→L+4 (2%) |
| 268    | 0.244         | HOMO→LUMO (25%), HOMO→L+1 (17%), HOMO→L+2 (14%) | H-3→LUMO (2%), H-1→LUMO (8%), H-1→L+3 (4%), H-1→L+5 (2%), HOMO→L+3 (7%), HOMO→L+4 (2%) |
| 266    | 0.002         | H-3→L+1 (10%), H-3→L+2 (11%), H-2→LUMO (18%), H-2→L+3 (25%), H-1→L+2 (10%) | H-1→L+1 (8%) |
| 258    | 0.029         | HOMO→L+4 (32%), HOMO→L+5 (22%) | H-5→L+1 (2%), H-3→L+2 (3%), H-3→L+4 (4%), H-3→L+5 (3%), |

Table S12. Results of TD-DFT calculations for 1-mqp-SBF (m06-2x/6-311+g(d, p)).
| No.  | Charge | Energy  | Transition Path | transitions |
|------|--------|---------|----------------|-------------|
| 257  | -1     | 0.094   | H-1→L+4 (10%), H-1→L+5 (11%), HOMO→L+4 (18%), HOMO→L+5 (16%) | H-1→L+4 (4%), HOMO→L+1 (3%), HOMO→L+2 (5%), HOMO→L+6 (3%) |
| 248  | -3     | 0.132   | H-3→LUMO (11%), H-3→L+3 (13%), H-1→LUMO (25%), H-1→L+3 (13%) | H-2→L+1 (5%), H-2→L+2 (6%), HOMO→LUMO (8%), HOMO→L+3 (3%) |
| 244  | -4     | 0.478   | H-4→L+1 (26%), H-2→L+2 (29%) | H-4→L+1 (3%), H-1→LUMO (3%), HOMO→LUMO (3%) |
| 243  | -2     | 0.105   | H-2→L+3 (13%) | H-9→L+1 (4%), H-9→L+2 (3%), H-6→L+1 (3%), H-6→L+2 (2%), H-5→L+1 (3%), H-5→L+2 (3%), H-4→L+1 (9%), H-4→L+2 (9%), H-2→L+1 (6%), H-2→L+2 (4%), H-1→LUMO (2%), HOMO→L+16 (3%), HOMO→L+17 (3%), HOMO→L+23 (3%) |
| 242  | -9     | 0.443   | H-9→L+1 (10%), H-9→L+2 (10%), H-10→L+1 (10%), H-10→L+2 (10%) | H-9→LUMO (2%), H-6→LUMO (9%), H-6→L+3 (2%), H-3→L+1 (4%), H-3→L+2 (5%), H-2→LUMO (9%), H-2→L+9 (2%), H-1→L+1 (4%), H-1→L+2 (4%) |
| 241  | -7     | 0.339   | H-7→LUMO (7%), H-7→L+3 (2%), H-6→L+1 (3%), H-6→L+2 (2%), H-5→L+1 (3%), H-5→L+2 (3%), H-4→L+1 (9%), H-4→L+2 (9%), H-2→L+1 (6%), H-2→L+2 (4%), H-1→L+1 (4%), H-1→L+2 (4%) |
| 238  | -10    | 0.089   | H-10→L+1 (10%), H-10→L+2 (10%) | H-10→L+1 (4%), H-10→L+2 (2%), H-10→L+3 (6%), H-10→L+9 (4%), H-7→L+13 (3%), H-2→L+10 (9%), H-2→L+11 (6%), H-2→L+13 (4%) |
| 237  | -8     | 0.011   | H-8→L+2 (11%) | H-8→LUMO (3%), H-8→L+1 |
| #   | 2→L+13 (18%) | (8%), H-8→L+3 (6%), H-8→L+9 (5%), H-7→L+10 (3%), H-7→L+13 (3%), H-2→L+10 (8%), H-2→L+12 (3%) |
|-----|--------------|-----------------------------------------------------------------------------------------------|
| 235 | H-3→LUMO (31%), H-1→LUMO (15%), H-1→L+3 (17%), HOMO→LUMO (15%) | HOMO→L+4 (4%) |
| 230 | H-3→L+1 (11%), H-1→L+1 (29%), H-1→L+2 (28%) | H-3→L+2 (6%), HOMO→L+2 (2%), HOMO→L+4 (5%), HOMO→L+5 (3%) |
| 226 | HOMO→LUMO (15%), HOMO→L+3 (20%), HOMO→L+5 (17%) | H-5→LUMO (3%), H-3→LUMO (2%), H-3→L+3 (2%), H-3→L+4 (3%), H-3→L+5 (2%), H-1→L+5 (3%), HOMO→L+4 (6%), HOMO→L+9 (4%) |
| 223 | H-1→L+5 (11%), HOMO→L+3 (22%), HOMO→L+4 (16%) | H-4→LUMO (4%), H-4→L+4 (3%), H-3→L+5 (4%), H-1→LUMO (4%), H-1→L+4 (6%), HOMO→L+5 (3%), HOMO→L+6 (2%) |
| 222 | H-3→L+4 (12%), H-1→L+4 (25%) | H-5→L+4 (2%), H-3→L+5 (4%), H-1→L+1 (7%), H-1→L+5 (9%), HOMO→L+1 (6%), HOMO→L+3 (3%), HOMO→L+4 (6%), HOMO→L+5 (9%) |
| 220 | H-3→L+1 (26%), H-3→L+2 (19%), H-1→L+1 (10%) | H-5→L+1 (3%), H-3→L+3 (3%), H-1→L+2 (9%), H-1→L+5 (2%), HOMO→L+3 (3%) |
| 218 | H-4→LUMO (17%), HOMO→L+1 (11%), HOMO→L+2 (14%), HOMO→L+3 (11%) | H-3→L+1 (5%), H-3→L+3 (6%), HOMO→L+5 (4%) |
Figure S9. Triplet spin density distribution (TD-DFT, B3LYP, 6-311+g(d, p), isovalue of 0.004) of 1-mqp-SBF.
Table S13. Atomic coordinates of 1-p-SBF at the fundamental state after geometry optimization (DFT b3lyp/6-31g(d)).

| Atom | X (Å)  | Y (Å)  | Z (Å)  |
|------|--------|--------|--------|
| C    | -0.739567 | -0.256958 | 0.035657 |
| C    | -0.686766  | 1.267294  | -0.169517 |
| C    | 0.421129   | 2.119334  | -0.280851 |
| C    | 0.170305   | 3.498049  | -0.4186  |
| H    | 1.019156   | 4.170533  | -0.506494 |
| C    | -1.126199  | 4.01336   | -0.454374 |
| H    | -1.276022  | 5.083687  | -0.568772 |
| C    | -2.224802  | 3.162897  | -0.338039 |
| H    | -3.236541  | 3.559603  | -0.353444 |
| C    | -1.99668   | 1.795182  | -0.188506 |
| C    | -2.959216  | 0.70361   | 0.002215  |
| C    | -4.354987  | 0.713561  | 0.060766  |
| H    | -4.910839  | 1.640791  | -0.053448 |
| C    | -5.028747  | -0.491004 | 0.270417  |
| H    | -6.114424  | -0.49943  | 0.318767  |
| C    | -4.318325  | -1.68791  | 0.419926  |
| H    | -4.856759  | -2.617419 | 0.584213  |
| C    | -2.921065  | -1.698696 | 0.359694  |
| H    | -2.371187  | -2.628933 | 0.474622  |
| C    | -2.250113  | -0.49924  | 0.151301  |
| C    | 0.034158   | -0.773268 | 1.252269  |
| C    | -0.071578  | -0.374825 | 2.579281  |
| H    | -0.758401  | 0.416899  | 2.867097  |
| C    | 0.721844   | -1.010405 | 3.54036   |
| H    | 0.651419   | -0.708161 | 4.581868  |
| C    | 1.603836   | -2.032679 | 3.17227   |
| H    | 2.213426   | -2.516774 | 3.930714  |
| C    | 1.708177   | -2.436777 | 1.839775  |
| H    | 2.39574    | -3.230647 | 1.559276  |
| C    | 0.918703   | -1.80249  | 0.878567  |
| C    | 0.815948   | -2.006886 | -0.57214  |
| C    | 1.478337   | -2.894181 | -1.422793 |
| H    | 2.212033   | -3.595131 | -1.032889 |
| C    | 1.186763   | -2.866179 | -2.788465 |
| H    | 1.696499   | -3.550388 | -3.467114 |
| C    | 0.241532   | -1.968285 | -3.297796 |
| H    | 0.022267   | -1.961758 | -4.362165 |
| C    | -0.427249  | -1.081319 | -2.446421 |
| H    | -1.165421  | -0.388298 | -2.841854 |
| C    | -0.129495  | -1.10127  | -1.089092 |
Number of imaginary frequency: 0

Table S14. Atomic coordinates of 1-\textbf{mbp-SBF} at the fundamental state after geometry optimization (DFT b3lyp/6-31g(d)).

| Atom | X (Å)    | Y (Å)    | Z (Å)    |
|------|----------|----------|----------|
| C    | 3.195224 | -0.287785| 0.731567 |
| C    | 1.496542 | -1.125757| -0.708814|
| C    | 3.62041  | -1.519827| 0.207895 |
| C    | 1.819465 | 1.444451 | -0.511437|
| C    | 2.571085 | -2.041272| -0.676357|
| C    | 1.808521 | 0.082465 | 0.190821 |
| C    | -2.002465| -0.819772| -0.813176|
| H    | -1.998883| -1.695637| -0.170952|
| C    | 0.348376 | -1.406783| -1.46091 |
| C    | 0.790361 | 0.329154 | 1.308559 |
| C    | -0.84668 | -0.507476| -1.539409|
| C    | 0.323254 | 1.656512 | 1.27144 |
| C    | 4.86357  | -2.048191| 0.564167 |
| H    | 5.199474 | -3.001154| 0.163203 |
| C    | 1.384639 | -3.518955| -2.14586 |
| H    | 1.32243  | -4.444255| -2.712449|
| C    | 2.560405 | 1.8427   | -1.617748|
| H    | 3.229608 | 1.146337 | -2.116564|
| C    | 4.000452 | 0.426477 | 1.611131 |
| H    | 3.67057  | 1.379745 | 2.015372 |
| C    | 0.962596 | 2.348205 | 0.144502 |
| C    | 0.316308 | -2.620829| -2.172308|
| H    | -0.56808 | -2.853032| -2.759169|
| C    | -3.167444| -0.042739| -0.91037 |
| C    | -4.378638| -0.388392| -0.122261|
| C    | 2.524992 | -3.235596| -1.395098|
| H    | 3.356429 | -3.934964| -1.365874|
Number of imaginary frequency: 0

| Atom | X (Å) | Y (Å) | Z (Å) |
|------|-------|-------|-------|
| C    | -3.806192 | -0.09749 | -0.342338 |
| C    | -2.062234 | -0.221466 | 1.271351 |
| C    | -4.382569 | 0.274956 | 0.926237 |
| C    | -1.70628 | 1.244863 | -0.839991 |

**Table S15.** Atomic coordinates of 1-mtp-SBF at the fundamental state after geometry optimization (DFT b3lyp/6-31g(d)).
|   |   |   |   |   |
|---|---|---|---|---|
| C | -3.307858 | -0.355987 | 1.922879 |
| C | -2.276851 | -0.044899 | -0.241422 |
| C | 1.252755 | -1.30427 | 1.13693 |
| H | 0.82212 | -2.280356 | 1.33828 |
| C | -0.869832 | -0.280376 | 2.003863 |
| C | -1.600346 | -1.106629 | -1.114926 |
| C | 0.497162 | -1.56706 | 1.40222 |
| C | -0.793968 | -0.501205 | -2.097279 |
| C | -5.770351 | -0.348766 | 1.068292 |
| H | -6.223762 | -0.486001 | 2.046733 |
| C | -2.200392 | -0.605711 | 4.035281 |
| H | -2.233267 | -0.754571 | 5.111302 |
| C | -1.953495 | 2.558993 | -0.461322 |
| H | -2.616378 | 2.780711 | 0.371187 |
| C | -4.603043 | 0.007825 | -1.476422 |
| H | -4.155983 | 0.145597 | -2.457281 |
| C | -0.858947 | 0.956096 | -1.926114 |
| C | -0.967093 | -0.477443 | 3.394013 |
| H | -0.050311 | -0.526682 | 3.975058 |
| C | 2.562464 | -1.213063 | 0.641426 |
| C | 3.360202 | -2.437987 | 0.371806 |
| C | -3.85176 | -0.54504 | 3.302467 |
| H | -4.347633 | -0.647476 | 3.796877 |
| C | -1.726891 | -2.488909 | -1.051897 |
| H | -2.356374 | -2.954169 | -0.297764 |
| C | -5.992384 | -0.066437 | -1.333537 |
| H | -6.62835 | 0.013963 | -2.211008 |
| C | -6.570403 | -0.243087 | -0.070895 |
| H | -7.651655 | -0.298496 | 0.023461 |
| C | -0.243342 | 1.990615 | -2.633423 |
| H | 0.416173 | 1.776668 | -3.470583 |
| C | -1.332776 | 3.593818 | -1.169716 |
| H | -1.511731 | 4.626324 | -0.882122 |
| C | 2.764552 | -3.5731 | -0.203951 |
| H | 1.715379 | -3.540278 | -0.483926 |
| C | 3.106242 | 0.060054 | 0.422424 |
| H | 4.120557 | 0.143749 | 0.043437 |
| C | -0.483629 | 3.310265 | -2.245359 |
| H | -0.00581 | 4.124753 | -2.782845 |
| C | -0.102053 | -1.285988 | -3.021883 |
| H | 0.525216 | -0.827461 | -3.781967 |
| C | 4.728568 | -2.492686 | 0.686289 |
| H | 5.202676 | -1.634967 | 1.155609 |
| Atom | X (Å)       | Y (Å)       | Z (Å)       |
|------|-------------|-------------|-------------|
| C    | 4.913519    | 0.694257    | 0.087912    |
| C    | 3.296388    | -0.555767   | 1.3055      |
| C    | 5.312244    | 0.63797     | 1.433644    |
| C    | 3.744658    | -1.171365   | -1.175317   |
| C    | 4.313307    | -0.129425   | 2.187451    |
| C    | 3.599227    | -0.068068   | -0.121425   |
| C    | -0.142349   | -1.060916   | 0.926392    |
| H    | -0.227641   | -0.157423   | 1.522886    |
| C    | 2.203081    | -1.288341   | 1.785561    |
| C    | 2.508148    | 0.805207    | -0.749291   |
| C    | 1.069364    | -1.762131   | 0.928881    |
| C    | 2.122587    | 0.293714    | -2.002762   |
| C    | 6.490429    | 1.263362    | 1.848734    |
| H    | 6.805465    | 1.224327    | 2.888445    |

Table S16. Atomic coordinates of 1-mqp-SBF at the fundamental state after geometry optimization (DFT b3lyp/6-31g(d)).
| C    | 3.177771 | -1.162843 | 4.02979 |
| H    | 3.114154 | -1.40968  | 5.086246 |
| C    | 4.593087 | -2.272064 | -1.16588 |
| H    | 5.259129 | -2.451469 | -0.325775 |
| C    | 5.681004 | 1.371077  | -0.85286 |
| H    | 5.371616 | 1.413792  | -1.893719 |
| C    | 2.890393 | -0.929969 | -2.267617 |
| C    | 2.165982 | -1.578182 | 3.162238 |
| H    | 1.323469 | -2.144628 | 3.549315 |
| C    | -1.250126 | -1.504704 | 0.187601 |
| C    | -2.519231 | -0.730586 | 0.189243 |
| C    | 4.263375 | -0.432234 | 3.547966 |
| H    | 5.05017  | -0.101387 | 4.220833 |
| C    | 1.934245 | 1.96812   | -0.249609 |
| H    | 2.238351 | 2.3654    | 0.715438 |
| C    | 6.86007  | 1.997678  | -0.436423 |
| H    | 7.470033 | 2.531441  | -1.16024 |
| C    | 7.260963 | 1.943192  | 0.90367 |
| H    | 8.180069 | 2.434819  | 1.211286 |
| C    | 2.877587 | -1.802674 | -3.357491 |
| H    | 2.218945 | -1.625569 | -4.203896 |
| C    | 4.575991 | -3.1473   | -2.257721 |
| H    | 5.232133 | -4.013602 | -2.263719 |
| C    | -2.498528 | 0.670689  | 0.13974 |
| H    | -1.544898 | 1.182282  | 0.054038 |
| C    | -1.12482  | -2.69253  | -0.550396 |
| H    | -1.961848 | -3.043583 | -1.147589 |
| C    | 3.724177  | -2.913361 | -3.34338 |
| H    | 3.723453  | -3.601197 | -4.184863 |
| C    | 1.149351  | 0.947104  | -2.761442 |
| H    | 0.842584  | 0.556517  | -3.728303 |
| C    | -3.759569 | -1.383064 | 0.219157 |
| H    | -3.78775  | -2.468085 | 0.254404 |
| C    | 0.957137  | 2.620622  | -1.010483 |
| H    | 0.493478  | 3.528124  | -0.633149 |
| C    | 1.16806   | -2.944977 | 0.183585 |
| H    | 2.100236  | -3.500949 | 0.177832 |
| C    | -4.964323 | -0.665633 | 0.20275 |
| C    | -3.685025 | 1.41789   | 0.12294 |
| C    | 0.568209  | 2.111733  | -2.255665 |
| H    | -0.193999 | 2.628368  | -2.832481 |
| C    | -4.909394 | 0.734912  | 0.155513 |
| H    | -5.833675 | 1.303394  | 0.196427 |
Table S17. Atomic coordinates of 1-p-SBF at the first triplet state after geometry optimization (TD-DFT b3lyp/6-31+g(d)).

| Atom | X (Å)    | Y (Å)    | Z (Å)    |
|------|----------|----------|----------|
| C    | -0.720545| -0.289692| 0.040585 |
| C    | -0.68181 | 1.239795 | -0.148443|
| C    | 0.389354 | 2.103582 | -0.243613|
| C    | 0.113902 | 3.508585 | -0.384025|
| H    | 0.951925 | 4.193691 | -0.468858|
| C    | -1.219644| 4.015626 | -0.437778|
| H    | -1.368417| 5.086059 | -0.557736|
| C    | -2.300502| 3.175462 | -0.341122|
| H    | -3.316869| 3.557238 | -0.377637|
| C    | -2.06172 | 1.755314 | -0.174715|
| C    | -2.960375| 0.715446 | 0.017287 |
| C    | -4.407065| 0.701997 | 0.095262 |
| H    | -4.969782| 1.623724 | -0.024066|
| C    | -5.048389| -0.493536| 0.324525 |
Table S18. Atomic coordinates of 1-mpb-SBF at the first triplet state after geometry optimization (TD-DFT b3lyp/6-31+g(d)).

| Atom | X (Å)     | Y (Å)     | Z (Å)     |
|------|-----------|-----------|-----------|
| C    | 3.207828  | -0.250218 | 0.735337  |
|   |   |   |   |
|---|---|---|---|
| C | 1.508522 | -1.172413 | -0.650547 |
| C | 3.638189 | -1.5077 | 0.278409 |
| C | 1.810881 | 1.408795 | -0.59268 |
| C | 2.5881 | -2.081105 | -0.573126 |
| C | 1.817381 | 0.083876 | 0.183387 |
| C | -1.991292 | -0.875691 | -0.766077 |
| C | -1.981117 | -1.708909 | -0.068632 |
| C | 0.360626 | -1.496596 | -1.388172 |
| C | 0.800665 | 0.385946 | 1.293469 |
| C | -0.838709 | -0.607314 | -1.516752 |
| C | 0.313066 | 1.762733 | 1.161285 |
| C | 4.886688 | -2.010343 | 0.658231 |
| H | 5.227597 | -2.982226 | 0.309292 |
| C | 1.407017 | -3.638999 | -1.965277 |
| H | 1.348281 | -4.592149 | -2.484603 |
| C | 2.532931 | 1.767797 | -1.701178 |
| H | 3.214425 | 1.064703 | -2.175022 |
| C | 4.013256 | 0.516302 | 1.572374 |
| H | 3.680996 | 1.48926 | 1.926174 |
| C | 0.904071 | 2.361641 | 0.057243 |
| C | 0.333883 | -2.745975 | -2.038185 |
| H | -0.54877 | -3.012118 | -2.614219 |
| C | -3.162248 | -0.112325 | -0.910553 |
| C | -4.372463 | -0.41698 | -0.101635 |
| C | 2.547499 | -3.312485 | -1.229531 |
| H | 3.381939 | -4.006521 | -1.165981 |
| C | 0.375639 | -0.415861 | 2.320878 |
| H | 0.745222 | -1.433687 | 2.423973 |
| C | 5.26299 | 0.013259 | 1.953808 |
| H | 5.903209 | 0.599695 | 2.607878 |
| C | 5.695433 | -1.240366 | 1.499076 |
| H | 6.668654 | -1.617142 | 1.803566 |
| C | 0.769978 | 3.692466 | -0.502095 |
| H | 0.099447 | 4.412654 | -0.041351 |
| C | 2.386272 | 3.080796 | -2.236219 |
| H | 2.954757 | 3.373548 | -3.113868 |
| C | -4.264614 | -0.767536 | 1.256154 |
| H | -3.284933 | -0.787602 | 1.726297 |
| C | -3.159442 | 0.940079 | -1.841914 |
| H | -4.044705 | 1.560364 | -1.955405 |
| C | 1.500593 | 4.021165 | -1.61967 |
| H | 1.410329 | 5.015853 | -2.04982 |
| C | -0.639363 | 2.263903 | 2.132121 |
Number of imaginary frequency: 0

| Atom | X (Å)     | Y (Å)     | Z (Å)     |
|------|-----------|-----------|-----------|
| C    | -3.821858 | -0.083155 | -0.317926 |
| C    | -2.068611 | -0.203036 | 1.284884  |
| C    | -4.392532 | -0.246031 | 0.956023  |
| C    | -1.712395 | 1.240834  | -0.84499  |
| C    | -3.311497 | -0.323824 | 1.946887  |
| C    | -2.292187 | -0.040106 | -0.228845 |
| C    | 1.242572  | -1.300524 | 1.138696  |
| H    | 0.803859  | -2.273233 | 1.341837  |
| C    | -0.870929 | -0.258263 | 2.011597  |
| C    | -1.626874 | -1.115474 | -1.100133 |
| C    | 0.495335  | -0.146325 | 1.403855  |
| C    | -0.796079 | -0.47962  | -2.12785  |
| C    | -5.781278 | -0.310155 | 1.107588  |
| H    | -6.231201 | -0.43605  | 2.089564  |
| C    | -2.191891 | -0.554574 | 4.057137  |
| H    | -2.218085 | -0.690746 | 5.135374  |
| C    | -1.937984 | 2.548081  | -0.499866 |
| H    | -2.59059  | 2.800697  | 0.333016  |
| C    | -4.625538 | 0.017258  | -1.449699 |
| H    | -4.184773 | 0.143604  | -2.435576 |
| C    | -0.845079 | 0.899596  | -1.978252 |

Table S19. Atomic coordinates of 1-mtp-SBF at the first triplet state after geometry optimization (TD-DFT b3lyp/6-31+g(d)).
| Atom | X         | Y         | Z         |
|------|-----------|-----------|-----------|
| C    | -0.960462 | -0.438106 | 3.405813  |
| H    | -0.040418 | -0.484101 | 3.983074  |
| C    | 2.555645  | -1.219251 | 0.646548  |
| C    | 3.347333  | -2.451523 | 0.384971  |
| C    | -3.38221  | -0.497226 | 3.330207  |
| H    | -4.341908 | -0.589572 | 3.832671  |
| C    | -1.757626 | -2.478997 | -1.044438 |
| H    | -2.382696 | -2.949293 | -0.288564 |
| C    | -6.016015 | -0.047048 | -1.298758 |
| H    | -6.657114 | 0.029643  | -2.173231 |
| C    | -6.588289 | -0.209366 | -0.029288 |
| H    | -7.669646 | -0.257314 | 0.071678  |
| C    | -0.215613 | 1.971151  | -2.724504 |
| H    | 0.436474  | 1.742219  | -3.562927 |
| C    | -1.307247 | 3.586611  | -1.244638 |
| H    | -1.475589 | 4.624728  | -0.974691 |
| C    | 2.74952   | -3.582159 | -0.199951 |
| H    | 1.702837  | -3.543809 | -0.48975  |
| C    | 3.109773  | 0.050292  | 0.425667  |
| H    | 4.125933  | 0.126137  | 0.049003  |
| C    | -0.452479 | 3.272089  | -2.348704 |
| H    | 0.018642  | 4.085781  | -2.894564 |
| C    | -0.102371 | -1.319017 | -3.084385 |
| H    | 0.523575  | -0.870615 | -3.850991 |
| C    | 4.712334  | -2.518682 | 0.716877  |
| H    | 5.18988   | -1.666236 | 1.193182  |
| C    | -1.06821  | -3.286828 | -1.995177 |
| H    | -1.172645 | -4.36734  | -1.962859 |
| C    | 1.075078  | 1.107948  | 1.176619  |
| H    | 0.490807  | 2.00342   | 1.364569  |
| C    | 5.454927  | -3.675564 | 0.472579  |
| H    | 6.506877  | -3.707059 | 0.745906  |
| C    | 3.491433  | -4.739623 | -0.443367 |
| H    | 3.010025  | -5.599259 | -0.903572 |
| C    | -0.249962 | -2.683784 | -3.002561 |
| H    | 0.263983  | -3.325201 | -3.714526 |
| C    | 4.847629  | -4.792266 | -0.108754 |
| H    | 5.424795  | -5.693782 | -0.298153 |
| C    | 2.386359  | 1.223733  | 0.686234  |
| C    | 2.996213  | 2.560052  | 0.449371  |
| C    | 2.776316  | 3.623743  | 1.342604  |
| C    | 3.813688  | 2.79497   | -0.670614 |
| C    | 3.352364  | 4.876707  | 1.124601  |
Number of imaginary frequency: 0

Table S20. Atomic coordinates of 1-mqp-SBF at the first triplet state after geometry optimization (TD-DFT b3lyp/6-31+g(d)).

| Atom | X (Å)   | Y (Å)   | Z (Å)   |
|------|---------|---------|---------|
| C    | 4.961549| 0.681482| 0.106073|
| C    | 3.306538|-0.509865| 1.330682|
| C    | 5.337151| 0.6607  | 1.460249|
| C    | 3.7848  | -1.204736|-1.127734|
| C    | 4.313763|-0.06987 | 2.218936|
| C    | 3.641246|-0.067845|-0.105327|
| C    | -0.150671|-1.005808| 0.939061|
| H    | -0.24329 | -0.09726 | 1.527895|
| C    | 2.192712 | -1.211771| 1.814122|
| C    | 2.568786 | 0.801054 | -0.777649|
| C    | 1.066568 | -1.700066| 0.954608|
| C    | 2.188135 | 0.214344 | -2.066877|
| C    | 6.518159 | 1.282417 | 1.877807|
| H    | 6.816338 | 1.270961 | 2.92352 |
| C    | 3.129483 | -1.027999| 4.07366 |
| H    | 3.042772 | -1.240925| 5.136198|
| C    | 4.609931 | -2.29901 | -1.097317|
| H    | 5.274225 | -2.473789| -0.253813|
| C    | 5.75526  | 1.319805 | -0.842344|
| H    | 5.465471 | 1.336192 | -1.890178|
| C    | 2.900398 | -0.959228| -2.27228 |
| C    | 2.126316 | -1.456945| 3.199616 |
| H    | 1.269409 | -2.00027 | 3.589846 |
| C    | -1.254885| -1.464977| 0.201562 |
| C    | -2.534431| -0.705368| 0.197381 |
| C    | 4.235617 | -0.328118| 3.588664 |
| H    | 5.014638 | 0.012773 | 4.266114 |
| C    | 2.012024 | 1.977896 | -0.348277|
| H    | 2.302535 | 2.417597 | 0.603397 |
| C    | 6.937277 | 1.943433 | -0.424843|
| H    | 7.567276 | 2.447073 | -1.15357 |
|   |   |   |   |
|---|---|---|---|
| C | 7.315075 | 1.923625 | 0.925065 |
| H | 8.236122 | 2.411794 | 1.233596 |
| C | 2.900744 | -1.904329 | -3.371643 |
| H | 2.249576 | -1.74609 | -4.226933 |
| C | 4.59465 | -3.216873 | -2.187746 |
| H | 5.245454 | -4.08598 | -2.171972 |
| C | -2.535276 | 0.696865 | 0.136779 |
| H | -1.589658 | 1.225112 | 0.05515 |
| C | -1.117703 | -2.658289 | -0.527917 |
| H | -1.948639 | -3.022322 | -1.126411 |
| C | 3.733085 | -2.997123 | -3.309514 |
| H | 3.744182 | -3.713989 | -4.12718 |
| C | 1.19968 | 0.894055 | -2.880367 |
| H | 0.896127 | 0.473427 | -3.835079 |
| C | -3.766141 | -1.376691 | 0.233202 |
| H | -3.778736 | -2.4619 | 0.280991 |
| C | 1.041779 | 2.630914 | -1.162994 |
| H | 0.59514 | 3.563713 | -0.832297 |
| C | 1.175631 | -2.8903 | 0.220843 |
| H | 2.109524 | -3.443945 | 0.227685 |
| C | -4.98232 | -0.677489 | 0.207743 |
| H | -3.734538 | 1.425333 | 0.110209 |
| C | 0.653974 | 2.069552 | -2.420985 |
| H | -0.091427 | 2.589 | -3.018171 |
| C | -4.949717 | 0.724125 | 0.144589 |
| H | -5.883002 | 1.279364 | 0.175465 |
| C | 0.086361 | -3.362511 | -0.514562 |
| H | 0.181305 | -4.281024 | -1.088352 |
| C | -6.278392 | -1.406127 | 0.266264 |
| C | -6.447195 | -2.515791 | 1.113453 |
| C | -7.369178 | -1.004647 | -0.525224 |
| C | -7.663053 | -3.199964 | 1.167426 |
| H | -5.626478 | -2.829633 | 1.75327 |
| C | -8.585689 | -1.68764 | -0.472142 |
| H | -7.255251 | -0.164506 | -1.205495 |
| C | -8.738458 | -2.789101 | 0.374716 |
| H | -7.772419 | -4.049784 | 1.836789 |
| H | -9.412286 | -1.363527 | -1.09978 |
| H | -9.685336 | -3.321278 | 0.41664 |
| C | -3.717758 | 2.911802 | 0.046691 |
| C | -2.796831 | 3.656958 | 0.804595 |
| C | -4.623587 | 3.611776 | -0.769972 |
| C | -2.781798 | 5.051977 | 0.748202 |
|   | X     | Y     | Z     |
|---|-------|-------|-------|
| H | -2.103547 | 3.138669 | 1.461894 |
| C | -4.60947  | 5.00676  | -0.82802 |
| H | -5.329294 | 3.056631 | -1.382646 |
| C | -3.688145 | 5.733849 | -0.0689  |
| H | -2.067683 | 5.607102 | 1.351776 |
| H | -5.314487 | 5.525464 | -1.473116 |
| H | -3.677283 | 6.819912 | -0.112631 |

Number of imaginary frequency: 0
5 Photophysical studies

Figure S10. UV-vis absorption spectra of 1-p-SBF, 1-mbp-SBF, 1-mtp-SBF and 1-mqp-SBF in cyclohexane.

Figure S11. Emission spectra at 298 K in cyclohexane of 1-p-SBF, 1-mbp-SBF, 1-mtp-SBF and 1-mqp-SBF.
Figure S12. Emission spectra at 77 K in 2Me-THF of 1-p-SBF, 1-mpb-SBF, 1-mtp-SBF and 1-mqp-SBF.

Figure S13. Absorption (cyclohexane, RT), fluorescence (cyclohexane, RT) and phosphorescence (2-MeTHF, 77 K) of 1-p-SBF.
Figure S14. Absorption (cyclohexane, RT), fluorescence (cyclohexane, RT) and phosphorescence (2-MeTHF, 77 K) of 1-mbp-SBF.

Figure S15. Absorption (cyclohexane, RT), fluorescence (cyclohexane, RT) and phosphorescence (2-MeTHF, 77 K) of 1-mtp-SBF.
Figure S16. Absorption (cyclohexane, RT), fluorescence (cyclohexane, RT) and phosphorescence (2-MeTHF, 77 K) of 1-mqp-SBF.

Figure S17. Determination of the molar absorption coefficient (cyclohexane, RT) of 1-mbp-SBF.
Figure S18. Determination of the molar absorption coefficient (cyclohexane, RT) of 1-mtp-SBF.

Figure S19. Determination of the molar absorption coefficient (cyclohexane, RT) of 1-
mqp-SBF.

| $\lambda_{\text{exc}}$ = 295 nm | Quinine sulfate in sulfuric acid | 1-mbp-SBF in cyclohexane |
|---------------------------------|---------------------------------|---------------------------|
| Slope                           | 1.42E+09                        | 9.55E+08                  |
| Refractive index                 | 1.336                           | 1.42662                    |
| Quantum yield                    | 0.546                           | 4.19E-01                   |
\( \lambda_{\text{exc}} = 295 \text{ nm} \)

|                        | Quinine sulfate in sulfuric acid | 1-mbp-SBF in cyclohexane |
|------------------------|----------------------------------|--------------------------|
| Slope                  | 6.33E+08                         | 4.54E+08                 |
| Refractive index       | 1.336                            | 1.42662                  |
| Quantum yield          | 0.546                            | 4.46E-01                 |

**Figure S20.** Determination of the quantum yield (cyclohexane, RT) of 1-mbp-SBF (2 measurements).
| $\lambda_{\text{exc}}$ = 290 nm | Quinine sulfate in sulfuric acid | 1-mtp-SBF in cyclohexane |
|-----------------------------|--------------------------------|----------------------------|
| Slope                      | 7.48E+08                       | 1.42E+08                   |
| Refractive index            | 1.336                          | 1.42662                    |
| Quantum yield               | 0.546                          | 1.18E-01                   |
\( \lambda_{\text{exc}} = 295 \text{ nm} \)

| Parameter                           | Value          |
|-------------------------------------|----------------|
| Quinine sulfate in sulfuric acid    |                |
| Slope                              | 6.33E+08       |
| Refractive index                    | 1.336          |
| Quantum yield                       | 0.546          |
| 1-mtp-SBF in cyclohexane            |                |
| Slope                              | 1.60E+08       |
| Refractive index                    | 1.42662        |
| Quantum yield                       | 1.57E-01       |

**Figure S21** Determination of the quantum yield (cyclohexane, RT) of 1-mtp-SBF (2 measurements).
$\lambda_{\text{exc}} = 295$ nm

| Quinine sulfate in sulfuric acid | 1-mqp-SBF in cyclohexane |
|---------------------------------|--------------------------|
| Slope                           | 6.33E+08                 | 1.50E+08                 |
| Refractive index                | 1.336                    | 1.42662                  |
| Quantum yield                   | 0.546                    | 1.47E-01                 |
Figure S22. Determination of the quantum yield (cyclohexane, RT) of 1-mqp-SBF (2 measurements).
Figure S23. Determination of the fluorescence lifetime (cyclohexane, RT) of 1-mbp-SBF (Top-Left), 1-mtp-SBF (Top-right) and 1-mqp-SBF (Bottom).
**Figure S24.** Spin-coated film (from a THF solution, C = 10mg/mL, room temperature). Left: Fluorescence spectrum, Right: Fluorescence decay curve. A/ 1-mbp-SBF, B/ 1-mtp-SBF, C/ 1-mqp-SBF, D/ 1-p-SBF (Lifetime is too short, < 1ns, to be measured).
Figure S25. Determination of the phosphorescence properties (2-MeTHF, 77 K) of 1-mbp-SBF.

Figure S26. Determination of the phosphorescence properties (2-MeTHF, 77 K) of 1-mtp-SBF.

Figure S27. Determination of the phosphorescence properties (2-MeTHF, 77 K) of 1-mbp-SBF.

Data of 1-p-SBF can be found in previous works.⁴
6 Electrochemical studies

Figure S28. CVs in oxidation recorded in CH$_2$Cl$_2$ + Bu$_4$NPF$_6$ 0.2 M, sweep-rate 100 mV s$^{-1}$. Platinum disk (Ø: 1mm) working electrode. a) (normalized at 405 mV) in presence of ferrocene as an internal probe (0.405 V vs SCE); b) (normalized at $E_{1\text{ox}}^i$) one cycle reaching only the first oxidation process and c) (normalized at $E_{1\text{ox}}^i$) one cycle reaching the second oxidation wave.
Figure S29. CVs in reduction recorded in DMF + Bu$_4$NPF$_6$ 0.1 M, sweep-rate 100 mV s$^{-1}$. Platinum disk (Ø: 1mm) working electrode. a) (normalized at E$_{1\text{red}}$) in presence of ferrocene as an internal probe (0.405 V vs SCE); b) (normalized at E$_{1\text{red}}$) one cycle reaching only the first oxidation process and c) (normalized at E$_{1\text{red}}$): one cycle reaching the second oxidation wave.
Figure S30. CV of 1-p-SBF in oxidation (3.87 \(10^3\) M) recorded in CH\(_2\)Cl\(_2\) + Bu\(_4\)NPF\(_6\) 0.2 M, sweep-rate 100 mV s\(^{-1}\). Platinum disk (Ø: 1mm) working electrode. a) One cycle reaching only the first oxidation; b) ten cycles between 0.27 and 1.97 V reaching the second oxidation wave showing the electrodeposition process and c) five cycles reaching only 1.86 V showing the reversible p-doping process of the deposit formed in the bottom-left.

Figure S31. CV of 1-p-SBF in reduction (3.3 \(10^3\) M) recorded in DMF + Bu\(_4\)NPF\(_6\) 0.1 M, sweep-rate 100 mV s\(^{-1}\). Platinum disk (Ø: 1mm) working electrode. a) One cycle in presence of ferrocene as internal reference reaching only the first reversible 1-p-SBF reduction process and b) one cycle reaching the two 1-p-SBF reduction processes.
**1-mbp-SBF**

**Figure S32.** CV of 1-mbp-SBF in oxidation (2.3 $10^{-3}$ M) recorded in CH$_2$Cl$_2$ + Bu$_4$NPF$_6$ 0.2 M, sweep-rate 100 mV s$^{-1}$. Platinum disk (Ø: 1mm) working electrode. a) One cycle reaching only the first oxidation; b) ten cycles reaching the second oxidation wave (electrodeposition process) and c) five cycles reaching only 1.54 V (the reversible p-doping process of the deposit).

**Figure S33.** CV of 1-mbp-SBF in reduction (5.1 $10^{-3}$ M) recorded in DMF + Bu$_4$NPF$_6$ 0.1 M, sweep-rate 100 mV s$^{-1}$. Platinum disk (Ø: 1mm) working electrode. a) One cycle in presence of ferrocene as internal reference reaching only the first reversible 1-mbp-SBF reduction process and b) one cycle reaching the two 1-mbp-SBF reduction processes.
- 1-mtp-SBF

Figure S34. CV of 1-mtp-SBF in oxidation (4.8 \times 10^{-3} \text{ M}) recorded in CH\textsubscript{2}Cl\textsubscript{2} + Bu\textsubscript{4}NPF\textsubscript{6} 0.2 M, sweep-rate 100 mV s\textsuperscript{-1}. Platinum disk (Ø: 1mm) working electrode. a) One cycle reaching only the first oxidation; b) ten cycles reaching the second oxidation wave up to 2.3 V (electrodeposition process); c) five cycles reaching only 1.6 V (the reversible p-doping process of the deposit); d) ten cycles reaching the second oxidation wave up to 2.09 V (electrodeposition process); e) five cycles reaching only 1.6 V (the reversible p-doping process of the deposit).
Figure S35. CV of 1-mtp-SBF in reduction ($3.85 \times 10^{-3}$ M) recorded in DMF + Bu$_4$NPF$_6$ 0.1 M, sweep-rate 100 mV s$^{-1}$. Platinum disk (Ø: 1mm) working electrode. a) One cycle in presence of ferrocene as internal reference reaching only the first reversible 1-mtp-SBF reduction process and b) one cycle reaching the two 1-mtp-SBF reduction processes.
Figure S36. CV of 9,9'-SBF in oxidation (2.22 \times 10^{-3} \text{ M}) recorded in CH₂Cl₂ + Bu₄NPF₆ 0.2 M, sweep-rate 100 mV s⁻¹. Platinum disk (Ø: 1mm) working electrode. a) One cycle reaching only the first 9,9'-SBF oxidation; b) ten cycles reaching the second 9,9'-SBF oxidation wave up to 2.28 V (electrodeposition process) and c) five cycles reaching only 1.88 V (the reversible p-doping process of the poly(9,9'-SBF) deposit).
- Biphenyl (BP)

**Figure S37.** CV of biphenyl in oxidation (7.5 $10^{-3}$ M) recorded in CH$_2$Cl$_2$ + Bu$_4$NPF$_6$ 0.2 M, sweep-rate 100 mV s$^{-1}$. Platinum disk (Ø: 1mm) working electrode. a) One cycle reaching only the first biphenyl oxidation; b) ten cycles reaching the second biphenyl oxidation wave up to 2.33 V (electrodeposition process) and c) five cycles reaching only 1.83 V (the reversible p-doping process of the poly(biphenyl) deposit).

**Figure S38.** CV of biphenyl in reduction (7.2 $10^{-3}$ M) recorded in DMF + Bu$_4$NPF$_6$ 0.1 M, sweep-rate 100 mV s$^{-1}$. Platinum disk (Ø: 1mm) working electrode. a) One cycle in presence of ferrocene as internal reference reaching only the first reversible biphenyl reduction process and b) one cycle reaching the two biphenyl reduction processes.
- *m*-terphenyl (*mTP*)

![Figure S39. CV of meta-terphenyl in oxidation (8.4 \(10^{-3}\) M) recorded in \(\text{CH}_2\text{Cl}_2 + \text{Bu}_4\text{NPF}_6\) 0.2 M, sweep-rate 100 mV s\(^{-1}\). Platinum disk (Ø: 1mm) working electrode. a) One cycle reaching 2.24 V; b) ten cycles reaching the second oxidation wave up to 2.03 V (electrodeposition process) c) five cycles reaching 1.64 V (reversible p-doping process of the deposit) d) ten cycles reaching only the first oxidation wave up to 1.83 V (electrodeposition process) and e) five cycles reaching 1.4 V (the reversible p-doping process of the deposit).]
Figure S40. CV of *meta*-terphenyl in reduction (3.9 $10^{-3}$ M) recorded in DMF + Bu$_4$NPF$_6$ 0.1 M, sweep-rate 100 mVs$^{-1}$. Platinum disk (Ø: 1 mm) working electrode.
- 1-mqp-SBF

Figure S41. a) CV of 1-mqp-SBF (1.8 x 10^{-3} M) in reduction recorded in DMF + Bu_4NPF_6 0.1 M in presence of ferrocene and b) CV of 1-mqp-SBF (1.8 x 10^{-3} M) in oxidation recorded in DCM + Bu_4NPF_6 0.2 M in presence of ferrocene. Sweep-rate 100 mV s^{-1}. Platinum disk (Ø: 1mm) working electrode.
7 Thermal properties

Figure S42. a) The TGA and b) DSC curves of 1-p-SBF, 1-mbp-SBF, and 1-mtp-SBF, where the $T_d$ were 272, 384, 387°C, and the $T_g$ were 49, 66, 90°C for 1-p-SBF, 1-mbp-SBF and 1-mtp-SBF, respectively.
8 Charge mobility

Space-charged limited current (SCLC) diodes. The device configuration of the hole-only device (HOD) is ITO/HAT-CN (10 nm)/Host (100 nm)/HAT-CN (10 nm)/Al (120 nm), and the electron-only device (EOD) is ITO/Liq (4 nm)/Host (100 nm)/Liq (4 nm)/Al (120 nm). After the fabrication, the devices were encapsulated before testing in dark.

Figure S43. The $J$–$V$ curves of hole-only (HOD) and electron-only (EOD) devices with host materials 1-p-SBF, 1-mpb-SBF, and 1-mtp-SBF, respectively. The $J$–$V$ curves of charge-only devices show the charge transport ability of the compounds. Based on the Schottky thermionic region and space-charge-limited current (SCLC) model, the curves can be divided into two parts under low bias. We assign the second region of the $J$–$V$ curve as assigned as the SCLC region, which then can be described by an equation:

$$J = \frac{9}{8} \varepsilon \varepsilon_0 \mu_0 \exp\left(\beta \frac{V}{L} \right) \frac{V^2}{L^3}$$

in which $V$ is the driving voltage, $L$ is the thickness of the thin layer, $\varepsilon_0$ is the permittivity of the free space, $\varepsilon$ is the relative dielectric constant (estimated to be 3.0 here), $\mu_0$ is the zero-field mobility and $\beta$ is Poole-Frenkel factor. The thickness $L$ equals to 100 nm, and the zero-field mobility of the compounds was calculated and summarized in Table 1 in the manuscript.
9 Devices characteristics

The configurations of devices are shown below:

Blue PhOLEDs: ITO/ HAT-CN (10 nm)/ TAPC (40 nm)/ TCTA (10 nm)/ mCP (10 nm)/ host: Flrpic (15 wt%, 20 nm)/ TmPyPB (40 nm)/ Liq (2 nm)/ Al (120 nm).

White PhOLEDs: ITO/ HAT-CN (10 nm)/ TAPC (40 nm)/ TCTA (10 nm)/ mCP (10 nm)/ host: Flrpic: PO-01 (1: 15 wt%: x wt%, 20 nm)/ Tm3Py26PyB (45 nm)/ Liq (2 nm)/ Al (120 nm).

Figure S44. Energy level alignment of the device and the molecular structures of materials in different layers.
Figure S45. Transient PL decay curves of the co-doped films (15 wt% Flrpic doped into three PHC host materials) for a) 1-p-SBF; b) 1-mpb-SBF; c) 1-mtp-SBF.

Figure S46. J-V curves of devices are based on three host materials with Tm3PyP26PyB and TmPyPB, respectively.
Figure S47. J-V-L curves (adg), CE-L and EQE-L curves (beh) and EL spectra (efi) at 5 mA/cm$^2$ of WOLEDs based on 1-p-SBF, 1-mbp-SBF and 1-mtp-SBF, respectively, with the doping ratios of PO-01 from 0.25 wt% to 1.5 wt% while keeping FIrpic 15 wt%.

Table S21. Detailed device performance of WOLEDs based on 1-p-SBF, 1-mbp-SBF and 1-mtp-SBF with the doping ratios of PO-01 from 0.25 wt% to 1.5 wt% while keeping FIrpic 15 wt%.

| Device | $V_{on}^{(a)}$ (V) | $CE^{(b)}$ (cd/A) | $PE^{(b)}$ (lm/W) | $EQE^{(b)}$ (%) | $\lambda_{max}^{(c)}$ (nm) | CIE (x, y)$^{(c)}$ |
|--------|------------------|------------------|-----------------|----------------|----------------|----------------|
| W1     |                  |                  |                 |                |                  |                |
| 0.25%  | 3.3              | 66.7/62.0/48.4   | 61.1/52.9/31.8  | 23.2/22.5/17.5 | 556             | (0.39, 0.45)  |
| 0.5%   | 3.3              | 73.3/69.3/63.1   | 66.6/58.6/45.2  | 24.5/23.6/21.4 | 556             | (0.42, 0.47)  |
| 1%     | 3.3              | 74.0/73.3/66.9   | 69.3/61.3/46.1  | 24.4/24.2/22.1 | 556             | (0.45, 0.48)  |
| 1.5%   | 3.3              | 78.0/75.3/68.8   | 68.9/62.5/46.6  | 25.4/24.6/22.4 | 556             | (0.46, 0.49)  |
| W2     |                  |                  |                 |                |                  |                |
| 0.25%  | 3.3              | 64.0/62.7/63.1   | 63.9/50.3/45.2  | 23.2/22.8/20.7 | 556             | (0.38, 0.45)  |
| 0.5%   | 3.3              | 75.0/70.7/65.2   | 67.9/59.5/47.3  | 25.3/24.2/22.3 | 556             | (0.42, 0.47)  |
| 1%     | 3.4              | 75.0/72.7/66.7   | 67.6/58.8/46.6  | 24.4/24.0/22.0 | 556             | (0.46, 0.49)  |
| 1.5%   | 3.4              | 75.0/70.7/64.7   | 67.6/57.3/45.1  | 23.8/23.2/21.2 | 560             | (0.47, 0.49)  |
| W3     |                  |                  |                 |                |                  |                |
| 0.25%  | 3.3              | 76.7/72.7/66.2   | 68.1/59.9/48.7  | 26.6/25.4/23.1 | 556             | (0.40, 0.46)  |
| 0.5%   | 3.3              | 82.0/78.7/71.7   | 75.9/66.4/53.9  | 27.7/26.6/24.2 | 556             | (0.42, 0.47)  |
| 1%     | 3.4              | 80.0/76.0/70.2   | 73.7/61.7/49.9  | 25.6/24.9/23.0 | 560             | (0.46, 0.49)  |
| 1.5%   | 3.4              | 76.7/73.3/67.5   | 68.9/60.9/49.1  | 24.7/23.8/21.9 | 560             | (0.48, 0.49)  |

a) The operating voltage at the onset. b) Values of CE, PE, and EQE at the maximum, 100 cd/m$^2$ and 1000 cd/m$^2$. c) Measured at a driving current density of 5 mA/cm$^2$. 

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Table S22. State-of-art device performance uses universal hosts in blue and white PhOLEDs.

| Compound | Blue PhOLEDs | White PhOLEDs (single emitting-layer) | Ref. |
|----------|--------------|---------------------------------------|------|
|          | EQE\text{max}/100/1000 [%] | CIE (x, y) | EQE\text{max}/100/1000 [%] | PE\text{max} [lm/W] | CIE (x, y) |      |
| 1-mtp-SBF | 25.6/24.1/21.7 | (0.14, 0.32) | 27.7/26.6/24.2 | 75.9/66.4/53.9 | (0.42, 0.47) | This work |
| m-DCz-S   | 25.1/23.5/13.6 | (0.15, 0.29) | 26.4/21.1/16.0 | 82.7/54.9/31.3 | (0.32, 0.46) | 11    |
| DCZppy    | -             | -          | 13.1/-12.2     | 17.3/-13.2    | (0.49, 0.45) | 12    |
| STDBT4    | 19.6/17.6/11.9 | (0.15, 0.38) | 23.7/22.7/17.5 | 65.0/54.1/26.5 | (0.39, 0.49) | 13    |
| BII-BCz   | 29.4/-28.2 (0.16, 0.33) | 25.2/-25.0 | 53.5/-47.6 | (0.34, 0.44) | 14    |
| BII-TPA   | 21.2/-16.5 (0.17, 0.34) | 20.0/-18.6 | 40.0/-30.9 | (0.30, 0.40) | 14    |
| POSTF     | 20.1/-19.2 (0.14, 0.30) | 25.0/-24.0 | 63.0/-46.4 | (0.35, 0.42) | 15    |
| BCz-Si    | 21.0/21.0/19.8 (0.16, 0.39) | 24.6/24.6/23.2 | 65.8/65.8/53.0 | (0.36, 0.47) | 16    |
| UGH2      | -             | -          | 12.0/-         | 26.4/-        | (0.43, 0.45) | 17    |
| mCPmPO    | 20.3/- (0.14, 0.32) | 17.6/-     | 39.7/-        | (0.34, 0.43) | 18    |
| mCP       | -             | -          | 19.3/-        | 42.5/-        | (0.33, 0.39) | 19    |
10 NMR spectra

10.1 1-mp-FO-\textsuperscript{1}H–CDCl\textsubscript{3}
10.2 1-mbp-FO-$^{13}$C–CDCl$_3$
10.3 1-mbp-SBF-\textsuperscript{1}H–CDCl\textsubscript{3}

![NMR spectrum]

10.4 1-bp-SBF–\textsuperscript{13}C–CDCl\textsubscript{3}

![NMR spectrum]
10.5 1-mtp-FO-¹H–CDCl₃

10.6 1-mtp-FO-¹³C–CDCl₃
10.7 1-mtp-SBF–$^1$H–CDCl$_3$

10.8 1-mtp-SBF–$^{13}$C–CDCl$_3$
10.9 1-mqp-FO-^1^H–CD₂Cl₂
10.10 1-mqp-FO–$^{13}$C–CD$_2$Cl$_2$

10.11 1-mqp-SBF–$^1$H–CD$_2$Cl$_2$
10.12 1-mqp-SBF–\textsuperscript{13}C–CD\textsubscript{2}Cl\textsubscript{2}
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