Substituents converting the molecular luminescence from thermally activated delayed fluorescence to ultralong room-temperature phosphorescence

Zetong Ma, Zhiqiang Yang, Lan Mu, Lisong Deng, Liangjian Chen, Bohan Wang, Xianfeng Qiao, Dehua Hu,* Bing Yang, Dongge Ma, Junbiao Peng and Yuguang Ma*
Materials and Measurements

$^1$H NMR, $^{13}$C NMR spectra were recorded in deuterated solvents on a Bruker AVANCE 400 MHz NMR Spectrometer. $^1$H NMR and $^{13}$C NMR chemical shifts are reported in ppm downfield from tetramethylsilane (TMS) reference using the residual protonated solvent as an internal standard. Mass spectra were determined on Waters ACQUITY TOD Mass Spectrometer.

Absorption spectra were measured with Shimadzu (UV-3600) UV-Vis-NIR spectrophotometer in a 1-cm quartz cell. Thermal gravity analysis (TGA) spectra were measured with NETZSCH TG 209 F3 Tarsus while differential scanning calorimetry (DSC) spectra were recorded on NETZSCH DSC 200 F3 Maia. Emission spectra were measured with SHIMADZU RF-5301pc or Edinburgh FLS980 or Horiba Fluoromax4 Spectrofluorometer. The absolute photoluminescence quantum yields of fluorescence were collected by HAMAMATSU Quantaurus-QY instrument in air. As for the PLQYs of phosphorescence, they were obtained according to the intensity proportion of the phosphorescent part to the total luminescence and the total luminescence quantum yield at the steady state. The integral area of fluorescence, phosphorescence and total luminescence were used as primary data. The data of transient fluorescence/phosphorescence decay spectra were determined with HAMAMATSU Quantaurus-Tau spectrometer C11367 or Edinburgh FLS980 spectrometer. Cyclic voltammetry (CV) was performed with a CHI620E electrochemical workstation using glassy carbon discs as the working electrode, Pt wire as the counter electrode, Ag/AgCl electrode as the reference electrode at a scanning rate of 100 mV/s. 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF$_6$) dissolved in CH$_2$Cl$_2$ or DMF was employed as the supporting electrolyte. The plot includes the signal of the ferrocene as an internal potential marker. CH$_2$Cl$_2$ was freshly distilled prior to use. Single crystals data collections were performed on XtaLAB P200 FR-X diffractometer, using Mo Kα radiation (0.71073 Å). Using Olex2, these structures were solved with the ShelXS and refined with the ShelXL-2014 refinement package using Least Squares minimization. Refinement was performed on $F^2$ anisotropically for all the non-hydrogen atoms by the full-matrix least-squares method. The hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters.

All chemicals were purchased from commercial suppliers (for example, J&K Corp.) and used without further purification unless otherwise specified.

Synthesis and Characterization

![Scheme S1. The synthetic routes towards benzo[5,6][1,4]thiazino[2,3,4-kl]phenothiazine 5,5,9,9-tetraoxide (BTPO) derivates.](image)

The starting material compound 1 and phthalimidesulfenyl chloride (PhtNSCl) was synthesized according to the previous literatures[1].

1) Compound 2:
To a solution of 4-bromo-N,N-bis(4-(tert-butyl)phenyl)aniline (1) (3 mmol, 1.31 g) in dry chloroform (60 mL) was added PhtNSCl (7.5 mmol, 1.60 g) under Ar atmosphere. The mixture was further stirring at 60 °C for 24 hours. Then the reaction solution was diluted with DCM, and was washed with a saturated NaHCO$_3$ solution and water twice. The organic layer was further dried with Na$_2$SO$_4$ and concentrated under reduced pressure, and then purified by column chromatography on silica gel with CH$_2$Cl$_2$/petroleum ether (4:1) to give compound 2 as light-yellow solid (62% yield, 1.471 g). $^1$H NMR (400 MHz, Chloroform-d) δ 7.94 (dd, J = 5.5, 3.1 Hz, 4H), 7.80 (dd, J = 8.4 Hz, 2H), 7.71 (dd, J = 8.4, 2.2 Hz, 2H), 7.33 – 7.27 (m, 2H), 7.19 (d, J = 2.2 Hz, 2H), 6.63 – 6.54 (m, 2H), 1.17 (s, 18H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 167.91, 150.22, 147.87, 141.04, 134.77, 133.12, 132.73, 131.95, 129.16, 126.88, 124.67, 124.00, 118.61, 112.61, 34.57, 31.08. MALDI-TOF MS (mass m/z): calcd for C$_{42}$H$_{38}$BrN$_2$O$_4$S$_2$Na$: 812.1223$, found 812.3427 [MNa$^+$.]

2) Compound 3:
To a solution of 4-bromo-N,N-bis(4-(tert-butyl)phenyl)aniline (1) (3 mmol, 1.31 g) in dry chloroform (60 mL) was added PhtNSCl (7.5 mmol, 1.60 g) under Ar atmosphere. The mixture was further stirring at 60 °C for 24 hours. Then the reaction solution was diluted with DCM, and was washed with a saturated NaHCO$_3$ solution and water twice. The organic layer was further dried with Na$_2$SO$_4$ and concentrated under reduced pressure, and then purified by column chromatography on silica gel with CH$_2$Cl$_2$/petroleum ether (4:1) to give compound 2 as light-yellow solid (62% yield, 1.471 g). $^1$H NMR (400 MHz, Chloroform-d) δ 7.94 (dd, J = 5.5, 3.1 Hz, 4H), 7.80 (dd, J = 8.4 Hz, 2H), 7.71 (dd, J = 8.4, 2.2 Hz, 2H), 7.33 – 7.27 (m, 2H), 7.19 (d, J = 2.2 Hz, 2H), 6.63 – 6.54 (m, 2H), 1.17 (s, 18H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 167.91, 150.22, 147.87, 141.04, 134.77, 133.12, 132.73, 131.95, 129.16, 128.88, 124.67, 124.00, 118.61, 112.61, 34.57, 31.08. MALDI-TOF MS (mass m/z): calcd for C$_{42}$H$_{38}$BrN$_2$O$_4$S$_2$Na$: 812.1223$, found 812.3427 [MNa$^+$.]
To a solution of compound 2 (1.5 mmol, 1.19 g) in dry DCM (60 mL) was added AlCl₃ (6 mmol, 1 g) under Ar atmosphere. The reaction mixture was stirred at room temperature and monitored by TLC. After the starting materials was disappeared, the mixture was diluted by DCM, and washed with a saturated Na₂CO₃ and water twice. The organic layer was further dried with Na₂SO₄ and concentrated under reduced pressure, and then purified by column chromatography on silica gel with petroleum ether to afford compound 3 as white solid (77% yield, 0.65 g). ¹H NMR (400 MHz, Chloroform-d) δ 7.32 (d, J = 2.2 Hz, 1H), 7.21 (d, J = 2.2 Hz, 1H), 7.16 (m, 3H), 7.12 – 7.02 (m, 3H), 7.01 (d, J = 2.0 Hz, 1H), 6.96 (d, J = 2.1 Hz, 1H), 1.30 (s, 9H), 1.25 (s, 9H). ¹³C NMR (126 MHz, CDCl₃) δ 129.92, 124.52, 123.56, 122.84, 121.41, 120.37, 119.75, 119.15, 118.59, 118.24, 116.59, 116.32, 134.63, 131.68, 130.50, 129.25, 128.93, 128.39, 126.89, 124.91, 124.56, 123.56, 121.70, 120.67, 118.71, 35.18, 31.09. MALDI-TOF MS (mass m/z): calcd for C₃₇H₃₆BrNO₃S: 559.05, found 559.51 [M⁺].

(3) Compound 4:

Compound 3 (1.15 mmol, 571mg) dissolved in AcOH (25 mL) was added 1.5 mL H₂O₂. The reaction mixture was heated at 100 ℃ for 4 hours. Quenched with 100 mL water, the precipitate was collected by filtration. Then the crude product was further purified by column chromatography on silica gel with DCM/petroleum ether (2:1) to give compound 4 as a white solid (72% yield, 465 mg).

(4) General procedure for the Suzuki coupling:

The schlenk flask was charged with compound 4 (1.43 mmol, 800 mg), respective boronic acid ester (4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline and 4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (1.3 equivalent, 1.86 mmol), K₂CO₃ (2.14 mmol, 296 mg) and THF/water (5:1 v/v, 40 mL/8 mL). After degassed by Ar, the mixture was added Pd(PPh₃)₄ (2.62 mmol, 0.80 g), and then purifed by column chromatography on silica gel with DCM/petroleum ether (2:1) to give compound 4 as a white solid (72% yield, 465 mg).

(5) BTPO:

The starting material Benz[5,6][1,4]thiazino[2,3,4-kl]phenothiazine (BTP) was synthesized according to the previous report[5]. 2 mL H₂O₂ was added to the solution of BTPO (2.62 mmol, 800 mg) in 30 mL AcOH. The reaction mixture was heated at 100 ℃ for 3 hours. Quenched with 100 mL water, the precipitate was collected by filtration. The target product was obtained from recrystallization from CH₂Cl₂/CH₂OH mixed solution as a white solid (91% yield, 968 mg). ¹H NMR (400 MHz, Chloroform-d) δ 8.36 (d, J = 2.2 Hz, 2H), 8.19 (dd, J = 7.8, 1.5 Hz, 2H), 7.73 – 7.66 (m, 3H), 7.63 (ddd, J = 8.8, 7.1, 1.6 Hz, 2H), 7.53 (ddd, J = 8.3, 7.2, 1.3 Hz, 2H). ¹³C NMR (101 MHz, Chloroform-d) δ 150.12, 149.15, 148.37, 147.30, 139.02, 137.61, 136.92, 134.81, 131.36, 130.95, 129.66, 129.42, 128.94, 128.64, 128.52, 128.64, 128.63, 124.55, 123.51, 122.22, 122.45, 121.88, 121.41, 120.47, 35.55, 35.14, 31.12. MALDI-TOF MS (mass m/z): calcd for C₂₆H₂₆BrNO₃S: 724.2429, found 724.4480 [M⁺].

Scheme S2. The synthetic routes towards benz[5,6][1,4]thiazino[2,3,4-kl]phenothiazine 5,5,9,9-tetraoxide (BTPO).

(5) BTPO:

The starting material Benz[5,6][1,4]thiazino[2,3,4-kl]phenothiazine (BTP) was synthesized according to the previous report[5]. 2 mL H₂O₂ was added to the solution of BTPO (2.62 mmol, 800 mg) in 30 mL AcOH. The reaction mixture was heated at 100 ℃ for 3 hours. Quenched with 100 mL water, the precipitate was collected by filtration. The target product was obtained from recrystallization from CH₂Cl₂/CH₂OH mixed solution as a white solid (91% yield, 968 mg). ¹H NMR (400 MHz, Chloroform-d) δ 8.36 (d, J = 7.8 Hz, 2H), 8.19 (dd, J = 7.8, 1.5 Hz, 2H), 7.73 – 7.66 (m, 3H), 7.63 (ddd, J = 8.4, 7.1, 1.6 Hz, 2H), 7.53 (ddd, J = 8.3, 7.2, 1.3 Hz, 2H). ¹³C NMR (101 MHz, Chloroform-d) δ 150.12, 149.15, 148.37, 147.30, 139.02, 137.61, 136.92, 134.81, 131.36, 130.95, 129.66, 129.42, 128.94, 128.64, 128.52, 128.64, 128.63, 124.55, 123.51, 122.22, 122.45, 121.88, 121.41, 120.47, 35.55, 35.14, 31.12. MALDI-TOF MS (mass m/z): calcd for C₂₆H₂₆BrNO₃S: 724.2429, found 724.4480 [M⁺].
MHz, CDCl$_3$ δ 139.48, 137.08, 133.55, 129.76, 129.18, 127.84, 126.40, 124.92, 124.35, 122.29. APCI (mass m/z): calcd for C$_{19}$H$_{13}$BrNO$_2$: 369.01, found 369.32 [M$^+$.]

Scheme S3. Molecular structure of reported RTP materials doped in polymer matrix with phosphorescence quantum yield and lifetime.
Figure S1. Distribution showing the relationship between RTP lifetime and quantum efficiency of reported monomeric RTP materials doped in different polymer matrix.

Table S1 Phosphorescence properties of reported RTP materials doped in polymer matrix.

| NO. | GUEST | HOST | \( \Phi_p \) (%) | \( T_p \) (S) | REFERENCE |
|-----|-------|------|------------------|-------------|-----------|
| 1   | Coronene | PMMA | 4                | 6           | J. Phys. Chem. 1967, 71, 4499. |
| 2   | d_{12}-Coronene | PMMA | 12               | 23          | J. Phys. Chem. 1967, 71, 4499. |
| 3   | MeOPh | PMMA | 3.1              | 0.23        | Angew. Chem. Int. Ed. 2016, 55, 9872. |
| 4   | MeO3Ph | PMMA | 3.9              | 0.23        | Angew. Chem. Int. Ed. 2016, 55, 9872 |
| 5   | Br6A | Isotactic PMMA | 7.5 | 1.90 \times 10^{-3} | J. Am. Chem. Soc. 2013, 135, 6325. |
| 6   | G1 | PVA 80 | 13 | 4.90 \times 10^{-3} | Angew. Chem. Int. Ed. 2014, 53, 11177. |
| 7   | BDPB | PMMA | 3.7              | 1.88        | Adv. Mater. 2020, 32, 2000880. |
| 8   | BDPB-Ac | PMMA | 5.4              | 0.75        | Adv. Mater. 2020, 32, 2000880 |
| 9   | BDPB-OH | PMMA | 5.4              | 1.74        | Adv. Mater. 2020, 32, 2000880 |
| 10  | BDPDPPT | PMMA | 2.7              | 2.15        | Adv. Mater. 2020, 32, 2000880 |
| 11  | TAT | PVA | 17.5             | 2.26        | Adv. Funct. Mater. 2020, 30, 2003693. |
| 12  | CTAT | PVA | 36.8             | 0.0721      | Adv. Funct. Mater. 2020, 30, 2003693. |
| 13  | SiAz | Zeonex | 7.5              | 0.032       | ACS Appl. Mater Interfaces 2021, 13, 2899 |
| 14  | TPD | PMMA | 4.6              | 0.7         | Adv. Mater. 2019, 31, 1807887. |
| 15  | BipyDpa | PMMA | <1               | 0.176       | Adv. Mater. 2019, 31, 1807887. |
| 16  | BipyTpa | PMMA | <1               | 0.28        | Adv. Mater. 2019, 31, 1807887. |
| 17  | PhenDpa | PMMA | 5.7              | 0.33        | Adv. Mater. 2019, 31, 1807887. |
| 18  | PhenTpa | PMMA | 1.2              | 0.68        | Adv. Mater. 2019, 31, 1807887. |
| 19  | TDI | PVA | 37.7             | 0.0289      | Adv. Funct. Mater. 2021, 31, 2010659. |
| 20  | MeTO | PVA | 24.5             | 0.02        | Adv. Funct. Mater. 2021, 31, 2010659. |
| 21  | HTO | PVA | 44               | 0.0105      | Adv. Funct. Mater. 2021, 31, 2010659. |
| 22  | FTO | PVA | 38               | 0.0174      | Adv. Funct. Mater. 2021, 31, 2010659. |
|   | Material | Polymer | Mass % | Tg °C | Reference |
|---|----------|---------|--------|-------|-----------|
| 23 | CTO      | PVA     | 39.7   | 0.0161| Adv. Funct. Mater. 2021, 31, 2010659. |
| 24 | BrTO     | PVA     | 26     | 0.0042| Adv. Funct. Mater. 2021, 31, 2010659. |
| 25 | BrPmDI   | PMMA    | 54.7   | 0.0014| Angew. Chem. Int. Ed. 2021, 60, 12323-12327 |
| 26 | IPmDI    | PMMA    | 2.4    | 6.3*10^6| Angew. Chem. Int. Ed. 2021, 60, 12323-12327 |
| 27 | PTzQ1    | PMMA    | 3.8    | 0.0055| Advanced Photonics Research 2021, 2, 2000201. |
| 28 | PTzQ2    | PMMA    | 2.5    | 0.0055| Advanced Photonics Research 2021, 2, 2000201. |
| 29 | (BzP)PB  | PMMA    | 50     | 0.208 | Appl. Phys. Lett. 2013 103, 093302 |
| 30 | IBF$_2$dbm-OCH$_3$ | PMMA | 9.8 | 0.0008 | J. Phys. Chem. A 2017, 121, 45, 8652–8658 |
| 31 | IBF$_2$dbm-F | PMMA | 8.7 | 0.0006 | J. Phys. Chem. A 2017, 121, 45, 8652–8658 |
| 32 | IBF$_2$dbm-CN | PMMA | 5.6 | 0.008 | J. Phys. Chem. A 2017, 121, 45, 8652–8658 |
| 33 | Zeonex   | 26     | 0.0343 | J. Mater. Chem. C 2017, 5, 6269-6280. |
| 34 | Zeonex   | 14     | 0.0298 | J. Mater. Chem. C 2017, 5, 6269-6280. |
| 35 | Zeonex   | 14     | 0.016  | Dyes Pigment. 2017, 142, 315-322. |
| 36 | Zeonex   | 21     | 0.0664 | Dyes Pigment. 2017, 142, 315-322. |
| 37 | Zeonex   | 11     | 0.088  | Dyes Pigment. 2017, 142, 315-322. |
| 38 | Zeonex   | 39     | 0.00105| Dyes Pigment. 2017, 142, 315-322. |
| 39 | Zeonex   | 2      | 0.0083 | Dyes Pigment. 2017, 142, 315-322. |
| 40 | Zeonex   | 2.9    | 0.0011 | Dyes Pigment. 2017, 142, 315-322. |
| 41 | Zeonex   | 1      | 0.0059 | Dyes Pigment. 2017, 142, 315-322. |
| 42 | BTPO-BCN | PMMA   | 11.6   | 0.822 | This work |
| 43 | BTPO-BCZ | PMMA   | 10.6   | 0.73  | This work |
| 44 | BTPO-TPA | PMMA   | 7.4    | 0.34  | This work |

**Thermodynamic properties**

Figure S2. TG curves and DSC curves (inset) of BTPO derivates.
High performance liquid chromatography spectra

Figure S3. High performance liquid chromatography spectra of BTPO and BTPO derivative.

Photophysical properties

Figure S4. Normalized absorption (solid line) and fluorescence spectra (dash dot line) of BTPO and BTPO derivates measured in $10^{-5}$ M toluene (a) and 5wt% doped in PMMA film(b).

Table S2. Photophysical properties of BTPO and BTPO derivates in air.

| Compound | $\lambda_{\text{abs}}$ / nm | $\lambda_{\text{em}}$ / nm | FWHM / nm | Stokes shift / nm |
|----------|----------------------------|---------------------------|------------|------------------|
| BTPO     | 346                        | 369                       | 34         | 23               |
| BTPO     | 344                        | 375                       | 40         | 29               |

$10^{-5}$ M in toluene | 5 wt% doped in PMMA film
| Derivative | Peak 1 | Peak 2 | Peak 3 | Peak 4 | Peak 5 | Peak 6 |
|------------|--------|--------|--------|--------|--------|--------|
| BTPO-BCN   | 360    | 377    | 28     | 17     | 356    | 380    | 39     | 24     |
| BTPO-BCZ   | 361    | 388    | 38     | 27     | 356    | 393    | 50     | 37     |
| BTPO-TPA   | 360    | 429    | 52     | 69     | 358    | 425    | 70     | 67     |

**Figure S5.** Steady PL and delayed PL spectra of BTPO derivatives measured in 10^{-3} M toluene at 77 K.
Figure S6. Steady PL and delayed PL spectra of BTPO derivatives measured in doped PMMA film at room temperature in vacuum.

Figure S7. The steady PL spectra measurements of BTPO derivative doped in PMMA with varied concentration at room temperature: (a) BTPO-BCN; (b) BTPO-BCZ and (c) BTPO-TPA.
Figure S8. Steady PL spectra of BTPO derivatives measured in doped PS film at room temperature in vacuum.

Figure S9. Transient fluorescence decay spectra of BTPO derivatives measured in 10^{-5} M toluene (a) and 5wt% doped in PMMA film(b) in air.

Table S3. Photophysical properties of BTPO derivatives.

| Compound   | 10^{-5} M in Tol measured at 77 K | 5 wt% doped in PMMA measured at room-temperature in vacuum |
|------------|----------------------------------|-------------------------------------------------------------|
|            | \( \lambda_n [nm] \) \( S_1 [eV] \) \( \lambda_{phos} [nm] \) \( T_1 [eV] \) \( \Delta E_{ST} [eV] \) | \( \lambda_n [nm] \) \( S_1 [eV] \) \( \lambda_{phos} [nm] \) \( T_1 [eV] \) \( \Delta E_{ST} [eV] \) |
| BTPO-BCN   | 373                              | 382                                          |
|            | 3.32                              | 3.25                                         |
|            | 477                               | 486                                          |
|            | 2.60                              | 2.55                                         |
|            | 0.72                              | 0.70                                         |
Table S4. Dynamic photophysical parameters of BTPO derivatives in doped PMMA film at room temperature.

| compound     | Fluorescence |                         |                         |                         | Phosphorescence |                         |                         |                         |
|--------------|--------------|--------------------------|--------------------------|--------------------------|----------------|--------------------------|--------------------------|--------------------------|
|              | $T_{\text{fluo}}/\text{ms}$ | $\phi_{\text{fluo}}/%$ | $k_{r(\text{fluo})}/10^7 \text{s}^{-1}$ | $k_{nr(\text{fluo})}/10^7 \text{s}^{-1}$ | $T_{\text{phos}}/\text{ms}$ | $\phi_{\text{phos}}/%$ | $k_{r(\text{phos})}/\text{s}^{-1}$ | $k_{nr(\text{phos})}/\text{s}^{-1}$ |
| BTPO-BCN     | 1.34         | 14.2                     | 10.60                    | 57.01                    | 7.01           | 822                      | 11.6                     | 0.114                    | 1.10                     |
| BTPO-BCZ     | 1.79         | 21.3                     | 11.90                    | 38.04                    | 5.92           | 730                      | 10.6                     | 0.145                    | 1.22                     |
| BTPO-TPA     | 3.28         | 29.4                     | 8.96                     | 19.27                    | 2.68           | 340                      | 7.4                      | 0.218                    | 2.72                     |

$k_{r(\text{fluo})} = \phi_{\text{fluo}}/T_{\text{fluo}}$; $k_{nr(\text{fluo})} = (1-\phi_{\text{fluo}})/T_{\text{fluo}}$; $k_{r(\text{phos})} = \phi_{\text{phos}}/T_{\text{phos}}$; $k_{nr(\text{phos})} = (1-\phi_{\text{phos}})/T_{\text{phos}}$.

The dynamic photophysical parameters of BTPO derivatives were calculated according to the previous reported methods\[^3, 4\] based on the quantum yields and lifetime of fluorescence and phosphorescence. Due to multiple heteroatoms (S, O, N) on such rigid interlocked scaffold along with excited states modulation, BTPO derivatives exhibit efficient ultralong room-temperature phosphorescence. Especially, the introduction of the sulfone group on the conjugated skeleton weakens the delocalization of electron pairs on the oxygen to π-conjugated skeleton, reducing the contribution of $(n, \pi^* )$ transition to triplet excited state. Combined with the further modification of the periphery groups, the triplet states of BTPO derivatives tend to present a much purer configuration of $(\pi, \pi^* )$, which conduce to long phosphorescence lifetimes of over 0.3 s and lower phosphorescent radiative decay rates for BTPO derivatives\[^3, 4\].

To be noted, an upward trend of phosphorescent radiative decay rate constants was observed from BTPO-BCN to BTPO-BCZ and further to BTPO-TPA, which is probably attributed to the increased proportion of $(n, \pi^* )$ transition caused by the lone electron pair of nitrogen atom in triplet excited state. As for the phosphorescent non-radiative decay rate constants, an ascending tendency as well was found from BTPO-BCN to BTPO-TPA. This may be due to the enhanced charge transfer characteristics for $T_1$ state along with more flexible substituents that might lead to greater vibrations in triplet configuration and cause more energy dissipation.

Figure S10. Steady PL and delayed PL spectra of BTPO measured in 10⁻⁵ M toluene (a) and 5wt% doped in PMMA film(b) at low temperature.

Table S5. Photophysical properties of BTPO at low temperature.

| Compound | 10⁻⁵ M in Tol measured at 77 K | 5 wt% doped in PMMA measured at 100 K in vacuum |
|----------|-------------------------------|-----------------------------------------------|
|          | $\lambda_c$ [nm] | $S_1$ [eV] | $\lambda_{\text{phos}}$ [nm] | $T_1$ [eV] | $E_{\text{AS}}$ [eV] | $\lambda_c$ [nm] | $S_1$ [eV] | $\lambda_{\text{phos}}$ [nm] | $T_1$ [eV] | $E_{\text{AS}}$ [eV] |
| BTPO     | 363 | 3.41 | 387 | 3.20 | 0.21 | 375 | 3.31 | 394 | 3.15 | 0.16 |
Figure S11. Steady PL spectra of BTPO 5wt% doped in PMMA film measured at varied temperature in vacuum.

![Figure S11](image1.png)

Figure S12. Fluorescence decay spectra of BTPO measured at 375nm in doped PMMA film in time range of 100 ns at 300 K in vacuum.

![Figure S12](image2.png)

Table S6. Lifetime of 5wt% BTPO doped in PMMA film in vacuum.

| Compound | $\tau_{prom}$ [ns] | $\tau_{delay}$ [μs] |
|----------|-------------------|-------------------|
| BTPO     | 1.04              | $\tau_{avg} = 41.04$, $t_1 = 6.29$, $t_2 = 103.66$ |
Figure S13. Fluorescence decay spectra of BTPO measured at 370nm in 5 wt% doped PMMA film in time range of 10 ms at varied temperature in vacuum
Figure S14. Normalized absorption and fluorescence spectra of BTPO-Ph measured in 10^{-5} M toluene (a) and 5wt% doped in PMMA film (c); Steady PL and delayed PL spectra of BTPO-Ph measured in 10^{-5} M toluene at 77 K (b) and in doped PMMA film at room temperature in vacuum (d); Fluorescence (e) and phosphorescence (f) decay spectra of BTPO-Ph measured at 369 nm in doped PMMA film at 300 K.

Table S7. Photophysical properties of BTPO derivatives.

| Compound | $\lambda_{	ext{abs}}$ [nm] | $\lambda_{	ext{fl}}$ [nm] | $\lambda_{	ext{phos}}$ [nm] | $\tau_{	ext{fluo}}$ [ns] | $\tau_{	ext{phos}}$ [ms] |
|----------|-----------------|-----------------|-----------------|-----------------|-----------------|
| BTPO-Ph  | 360             | 382             | 456             | 359             | 658             |

| Compound | $\lambda_{	ext{abs}}$ [nm] | $\lambda_{	ext{fl}}$ [nm] | $\lambda_{	ext{phos}}$ [nm] | $\tau_{	ext{fluo}}$ [ns] | $\tau_{	ext{phos}}$ [ms] |
|----------|-----------------|-----------------|-----------------|-----------------|-----------------|
| BTPO-Ph  | 360             | 382             | 456             | 359             | 658             |
Figure S15. (a) Steady PL spectra of BTPO-BCN measured in doped PMMA film coated by PVA layer at room temperature under ambient condition an in vacuum.
(b) PL decay profile of BTPO-BCN measured in doped PMMA film coated by PVA layer at room temperature in vacuum.

Table S8. Dynamic photophysical parameters of BTPO derivatives in doped PMMA film coated by PVA at room temperature.

| compound   | Fluorescence | Phosphorescence |
|------------|--------------|-----------------|
|            | $T_{flu}$/ns | $\phi_{flu}$/% | $k_{r(fluo)}/10^{7}$ s$^{-1}$ | $k_{nr(fluo)}/10^{7}$ s$^{-1}$ | $k_{(ISC)}/10^{7}$ s$^{-1}$ | $T_{phos}$/ms | $\phi_{phos}$/% | $k_{r(phos)}/$s$^{-1}$ | $k_{nr(phos)}/$s$^{-1}$ |
| BTPO-BCN   | 1.28         | 14.50          | 11.33             | 60.07                        | 6.72                         | 743           | 8.6             | 0.116             | 1.23                        |

$k_{r(fluo)} = \phi_{flu}/T_{flu}; k_{nr(fluo)} = (1 - \phi_{flu} - \phi_{phos})/T_{flu}; k_{(ISC)} = \phi_{phos}/T_{flu}; k_{r(phos)} = \phi_{phos}/T_{phos}; k_{nr(phos)} = (1 - \phi_{phos})/T_{phos}$.

Theoretical Calculation

The excitation energy and natural transition orbitals (NTO) were evaluated at TD-M062X/6-31G (d, p) level by Gaussian 09 program. At the same level, the oscillator strengths $f$ and spin-orbit coupling (SOC) were evaluated using BDF program.
Figure S16. Calculated molecular structure and frontier orbitals (FMOs) of BTPO and BTPO derivatives.

Figure S17. Calculated energy level diagrams of BTPO and BTPO derivatives.
Figure S18. Natural transition orbitals of BTPO and BTPO derivatives.

Table S9. Spin-orbit coupling (SOC) constants of BTPO and BTPO derivatives.

| Compound   | \(<S_0|\hat{H}_{\text{SO}}|T_1>\) | \(<S_0|\hat{H}_{\text{SO}}|T_2>\) | \(<S_0|\hat{H}_{\text{SO}}|T_3>\) | \(<S_0|\hat{H}_{\text{SO}}|T_4>\) | \(<S_0|\hat{H}_{\text{SO}}|T_5>\) |
|------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|
| BTPO       | 2.049                           | 0.008                           | 1.155                           | 1.358                           | 3.085                           |
| BTPO-BCN   | 1.013                           | 0.303                           | 0.300                           | 0.399                           | 0.565                           |
| BTPO-BCZ   | 1.000                           | 0.425                           | 0.282                           | 0.319                           | 0.777                           |
| BTPO-TPA   | 1.035                           | 0.349                           | 0.148                           | 0.311                           | 0.196                           |

Solvatochromic effect

The properties of ground state \(S_0\) and the lowest singlet excited state \(S_1\) can be better understood through solvatochromic experiment. We use the Lippert-Mataga equation to explore the influence of solvent environment on the optical property of our materials, the model can describe the interaction between the solvent and the dipole moment of solute:

\[
hc(v_a - v_f) = hc\left(v_0^b - v_f^b\right) - \frac{2(\mu_e - \mu_g)^2}{a^3}f(\epsilon, n)
\]

where \(f\) is the orientational polarizability of the solvent, \(v_0^b - v_f^b\) corresponds to the Stokes shifts when \(f\) is zero, \(\mu_e\) is the excited state dipole moment, \(\mu_g\) is the ground-state dipole moment; \(a\) is the solvent cavity (Onsager) radius, derived from the Avogadro number \(N\), molecular weight \(M\), and density \(d = 1.0\ \text{g cm}^{-3}\); \(\epsilon\) and \(n\) are the solvent dielectric and the solvent refractive index, respectively; \(f(\epsilon, n)\) and \(a\) can be calculated respectively as follows:
\[ \alpha = \left( \frac{3M}{4N\pi d} \right)^{1/3} \]

Figure S19. Normalized absorption (right) and fluorescence (left) spectra of BTPO-BCN measured in different solvents.

Table S10. Detailed absorption and emission peak positions of BTPO-BCN in different solvents.

| Solvent   | n   | \( \varepsilon \) | \( f(\varepsilon, n) \) | \( \lambda_{\text{abs}} \) [nm] | \( \lambda_{\text{em}} \) [nm] | FWHM [nm] | Stokes shift [nm] | \( \nu_a - \nu_f \) [cm\(^{-1}\)] |
|-----------|-----|-------------------|--------------------------|----------------|----------------|-----------|------------------|-------------------|
| Hexane    | 1.375 | 1.9 | 0.0012 | 356 | 368 | 24 | 12 | 916 |
| Toluene   | 1.497 | 2.38 | 0.014 | 360 | 377 | 28 | 17 | 1253 |
| Butyl ether | 1.399 | 3.08 | 0.096 | 357 | 372 | 28 | 15 | 1129 |
| Isopropyl ether | 1.368 | 3.88 | 0.145 | 356 | 372 | 28 | 16 | 1208 |
| Diethyl ether | 1.352 | 4.34 | 0.167 | 356 | 375 | 31 | 19 | 1423 |
| EtOAc     | 1.372 | 6.02 | 0.2 | 357 | 381 | 37 | 24 | 1764 |
| THF       | 1.407 | 7.58 | 0.21 | 358 | 382 | 37 | 24 | 1755 |
| DCM       | 1.424 | 8.93 | 0.217 | 359 | 380 | 34 | 21 | 1539 |
| Acetone   | 1.359 | 20.7 | 0.284 | 356 | 387 | 47 | 31 | 2250 |
| MeCN      | 1.344 | 37.5 | 0.305 | 360 | 392 | 52 | 32 | 2268 |
Figure S20. Normalized absorption (right) and fluorescence (left) spectra of BTPO-BCZ measured in different solvents.

Table S11. Detailed absorption and emission peak positions of BTPO-BCZ in different solvents.

| Solvent   | n   | ε   | f(ε, n) | λ<sub>max</sub> [nm] | λ<sub>em</sub> [nm] | FWHM [nm] | Stokes shift [nm] | ν<sub>a</sub>-ν<sub>f</sub> [cm<sup>-1</sup>] |
|-----------|-----|-----|---------|----------------------|---------------------|-----------|------------------|------------------|
| Hexane    | 1.375 | 1.9 | 0.0012  | 359                  | 377                 | 29        | 18               | 1330             |
| Toluene   | 1.497 | 2.38| 0.014   | 361                  | 388                 | 38        | 27               | 1928             |
| Butyl ether | 1.399 | 3.08| 0.096   | 359                  | 384                 | 37        | 25               | 1813             |
| Isopropyl ether | 1.368 | 3.88| 0.145   | 357                  | 386                 | 40        | 29               | 2104             |
| Diethyl ether | 1.352 | 4.34| 0.167   | 357                  | 390                 | 47        | 33               | 2370             |
| EtOAc     | 1.372 | 6.02| 0.2     | 358                  | 400                 | 58        | 42               | 2933             |
| THF       | 1.407 | 7.58| 0.21    | 358                  | 407                 | 63        | 49               | 3363             |
| DCM       | 1.424 | 8.93| 0.217   | 358                  | 417                 | 71        | 59               | 3952             |
| Acetone   | 1.359 | 20.7| 0.284   | 358                  | 436                 | 115       | 78               | 4997             |
| MeCN      | 1.344 | 37.5| 0.305   | 357                  | 479                 | 158       | 122              | 7134             |

Figure S21. Normalized absorption (right) and fluorescence (left) spectra of BTPO-TPA measured in different solvents.

Table S12. Detailed absorption and emission peak positions of BTPO-TPA in different solvents.

| Solvent   | n   | ε   | f(ε, n) | λ<sub>max</sub> [nm] | λ<sub>em</sub> [nm] | FWHM [nm] | Stokes shift [nm] | ν<sub>a</sub>-ν<sub>f</sub> [cm<sup>-1</sup>] |
|-----------|-----|-----|---------|----------------------|---------------------|-----------|------------------|------------------|
| Hexane    | 1.375 | 1.9 | 0.0012  | 359                  | 401                 | 38        | 42               | 2917             |
| Toluene   | 1.497 | 2.38| 0.014   | 360                  | 429                 | 52        | 69               | 4468             |
| Butyl ether | 1.399 | 3.08| 0.096   | 359                  | 425                 | 53        | 66               | 4326             |
| Isopropyl ether | 1.368 | 3.88| 0.145   | 358                  | 436                 | 61        | 78               | 4997             |
| Diethyl ether | 1.352 | 4.34| 0.167   | 359                  | 448                 | 70        | 90               | 5534             |
| EtOAc     | 1.372 | 6.02| 0.2     | 358                  | 472                 | 91        | 114              | 6747             |
|        | f | 7.58 | 0.21 | 358 | 487 | 97 | 129 | 7399 |
|--------|---|------|------|-----|-----|----|-----|------|
| THF    |   | 1.407|      |     |     |    |     |      |
| DCM    |   | 1.424|      |     |     |    |     |      |
| Acetone|   | 1.359|      |     |     |    |     |      |
| MeCN   |   | 1.344|      |     |     |    |     |      |

**Figure S22.** Linear correlation of orientational polarization (f) of solvent media with the Stokes shift (νa-νf; a: absorbed light; f: fluorescence) for BTPO derivatives.

**Phosphorescence graph**
**Figure S23.** Photographs of (a) BTPO-derivates in PMMA film in vacuum and (b) BTPO-BCN in PMMA film covered by PVA in air under UV lamp and after the removal of UV source.

**Supplementary Video**

**Video 1.** When excited by a 365 nm UV lamp, 5wt% BTPO-BCN doped in PMMA film exhibited bluish-green luminescence. After removal of the light source, the emission color turned green, easily observed by the naked eyes.

**Video 2.** When excited by a 365 nm UV-lamp, 5wt% BTPO-BCZ doped in PMMA film exhibited blue luminescence. After the removal of the emission color turned green, easily observed by the naked eyes.

**Video 3.** When excited by a 365 nm UV-lamp, 5wt% BTPO-TPA doped in PMMA film exhibited blue luminescence. After the removal of the emission color turned green, easily observed for several seconds by the naked eyes.

**Video 4.** When excited by a 365 nm UV lamp, 5wt% BTPO-BCN doped in PMMA film covered by a PVA layer exhibited bluish-green luminescence under ambient condition. After removal of the light source, the emission color turned green, easily observed by the naked eyes.

**Video 5.** When excited by a 365 nm UV lamp, the pattern exhibited cyan-blue luminescence. After removal of the light source, the emission color turned green, easily observed by the naked eyes.

**Video 6.** When excited by a 365 nm UV lamp, the pattern of SCUT exhibited cyan-blue luminescence. After removal of the light source, the emission color turned green, easily observed by the naked eyes.

**Electrochemical properties**
Figure S24. Cyclic voltammetry spectra of BTPO derivates measured in DMF (a) and DCM (b).

Figure S25. Cyclic voltammetry spectra of BTPO measured in DMF.

Table S13. Electrochemical properties of BTPO and BTPO derivates.

| Compound     | \(E_{\text{LUMO}}/\text{eV}\) | \(E_{\text{HOMO}}/\text{eV}\) | \(E_g/\text{eV}\) |
|--------------|-------------------------------|-------------------------------|-----------------|
| BTPO-BCN     | -2.76                         | -6.03                         | 3.27            |
| BTPO-BCZ     | -2.73                         | -5.62                         | 2.89            |
| BTPO-TPA     | -2.73                         | -5.26                         | 2.53            |
| BTPO         | -2.77                         | -6.17                         | 3.40            |

[a] Estimated from the onset potential of the first reduction wave and calculated according to \(E_{\text{LUMO}} = -(4.8 + E_{\text{onset}})\) eV. [b] Estimated from the onset potential of the first oxidation wave and calculated according to \(E_{\text{HOMO}} = -(4.8 + E_{\text{onset}})\) eV. [c] Calculated according to \(E_g = (E_{\text{LUMO}} - E_{\text{HOMO}})\) eV. [d] \(E_{\text{HOMO}} = E_{\text{LUMO}} - E_g\). [e] \(E_g = 1240 / \lambda_{\text{onset}}\).

The electrochemical properties of BTPO and BTPO derivates were investigated by cyclic voltammetry (CV) measurement. Observed in Figure S24a and S25, BTPO, BTPO-BCZ and BTPO-TPA exhibited one well-defined reversible reduction peak, while BTPO-BCN shows two reversible reduction peaks as a result of the introduction of the withdrawing functional group of benzonitrile. The LUMO levels of all the compounds estimated from the onset potential of the first reduction wave are -2.77 eV for BTPO, -2.76 eV for BTPO-BCN, -2.73 eV for BTPO-BCZ and -2.73 eV for BTPO-TPA, respectively. It indicated minor changes occurred on the distribution of LUMOs that remained mainly at the BTPO core, confirmed by the calculation results of the frontier orbitals. With the increased electron-donating character of substituents from BCN to BCZ, and further to TPA, the HOMO energy levels were uplifted to -6.03 eV for BTPO-BCN, -5.62 eV for BTPO-BCZ and -5.26 eV for BTPO-TPA, as compared with -6.17 eV for BTPO. Correspondingly, the
distribution of HOMOs for BTPO derivatives delocalized to the periphery groups instead of the BTPO core. The above results lead to narrower bandgaps for BTPO derivatives.

**X-ray Crystallographic Analysis**

Crystalllographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication. The single crystal X-ray crystallographic data were summarized in Table S13.

**Table S14.** Single-crystal XRD data

| Compound | BTPO-BCN |
|----------|----------|
| CCDC number | 2079614 |
| Empirical formula | C33H30N2O4S2 |
| Formula weight | 582.71 |
| Crystal system | Monoclinic |
| Space group | C1 2/c 1 |
| a (Å) | 27.3326(6) |
| b (Å) | 13.6010(4) |
| c (Å) | 16.1847(3) |
| α (°) | 90 |
| β (°) | 93.524(2) |
| γ (°) | 90 |
| Volume (Å³) | 6005.3 |
| Density (mg/m³) | 1.289 |
| Crystal size (mm³) | 0.1×0.08×0.06 |
| Z | 8 |
| Data/restraints/parameters | 5294/0/376 |
| Goodness-of-fit | 1.028 |
| Final R [I>2sigma(I)] | R1=0.0454, wR2=0.1130 |
| R indices (all data) | R1=0.0596, wR2=0.1198 |
Figure S26. Crystal structure and packing arrangement of BTPO-BCN.

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NMR Spectra
