Supporting Information

Fulleretic Well-Defined Scaffolds: Donor–Fullerene Alignment Through Metal Coordination and Its Effect on Photophysics

Derek E. Williams, Ekaterina A. Dolgopolova, Danielle C. Godfrey, Evgeniya D. Ermolaeva, Perry J. Pellechia, Andrew B. Greytak, Mark D. Smith, Stanislav M. Avdoshenko, Alexey A. Popov,* and Natalia B. Shustova*

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Materials. Malonyl dichloride (97%, Acros Organics), 4-pyridylcarbinol (98%, Matrix Scientific), tetrakis(4-carboxyphenyl)porphyrin (97%, Frontier Scientific), silver hexafluorophosphate (99%, Strem Chemicals Inc.), benzene (ACS grade, EMD Chemicals), methanol (ACS grade, BDH), acetonitrile (HPLC grade, Fisher Scientific), benzonitrile (99%, Alfa Aesar), triethylamine (reagent grade, Fisher Scientific), anhydrous sodium sulfate (ACS grade, Amresco), acetone (ACS grade, Fisher Scientific), C$_6$0 (>99.5%, Solaris Chemicals), iodine (ACS grade, EMD Chemicals), toluene (ACS grade, Oakwood Chemicals), DBU [(1,8-diazabicyclo[5.4.0]undec-7-ene), (98%, Acros Organics)], chloroform (ACS grade, Macron Chemicals), Zn(NO$_3$)$_2$·6H$_2$O (technical grade, Ward’s Science), ethanol (Decon Laboratories, Inc.), N,N-diethylformamide (>99%, TCI America), tetrahydrofuran (ACS grade, EMD Chemicals), dichloromethane (ACS grade, BDH), and DMSO-$d_6$ (Cambridge Isotopes) were used as received. The compound bis(pyridin-4-ylmethyl)malonate (S2) was prepared according to the reported procedure.$^{[1]}$

Synthesis of bis(pyridin-4-ylmethyl)-3'H-cyclopropa-[1,2](C$_{60}$-$J_h$)[5,6]fullerene-3',3'-dicarboxylate (C$_{75}$H$_{12}$N$_2$O$_4$, BPCF). Preparation of BPCF was performed based on the reported procedure (Scheme S1).$^{[1]}$ The crystals of BPCF suitable for single-crystal X-ray analysis were grown from a saturated toluene solution (see more details in the crystallographic section). To get the structural information necessary for the simulation of the crystal structure of 1, BPCF (0.8 mg, 0.80 µmol) in 0.8 mL benzene was layered over AgPF$_6$ (0.24 mg, 0.95 µmol) in 0.32 mL MeOH/benzonitrile 1:3 in a 5 mm NMR tube, and left at room temperature for 9 days. As a result, the crystal structure of the Ag$_2$(BPCF)$_2$(PF$_6$)$_2$ molecular complex was obtained (Figure S1). IR (neat, cm$^{-1}$): 672, 687, 704, 711,739, 745, 755, 775, 788, 791,816, 821,834, 885, 1007, 1064, 1099, 1114, 1174, 1186, 1198, 1207, 1226, 1244, 1251, 1267, 1426, 1430, 1477, 1618, and 1752, 2238, 3033 (Figure S13). Furthermore, another fullerene-containing crystal structure was obtained by layering AgPF$_6$ (0.24 mg, 0.95 µmol) in 0.24 mL acetonitrile over BPCF (0.8 mg, 0.80 µmol) in 0.8 mL benzene. Single crystals of the two-dimensional Ag(BPCF)$_2$(PF$_6$) coordination network were obtained. IR (neat, cm$^{-1}$): 674, 704, 712, 739, 756, 761, 766, 777, 806, 817, 832, 866, 875, 1001, 1005, 1113, 1135, 1175, 1188, 1202, 1232, 1252, 1266, 1274, 1291, 1422, 1428, 1614, 1743, 2352, 2932, 3034, 3090. Figures S14 and S15 show the FT-IR spectrum and powder X-ray diffraction pattern, respectively.
Scheme S1. Synthesis of BPCF (TEA = triethylamine, DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene).

Preparation of 1 ([Zn$_2$(ZnTCPP)(BPCF)$_{0.23}$·(DEF)$_{0.77}$]·2EtOH·0.2H$_2$O, Zn$_3$C$_{73.1}$H$_{47.6}$N$_{5.23}$O$_{11.9}$).

In a one-dram vial, Zn(NO$_3$)$_2$·6H$_2$O (3.6 mg, 12 µmol), H$_4$TCPP (3.3 mg, 4.2 µmol), and BPCF (4.3 mg, 4.3 µmol) were dissolved in 0.85 mL of a DEF/EtOH (3:1) mixture followed by brief sonication. The mixture was filtered and the resulting solution was heated at 80 °C for 16 h in an isothermal oven. After 16 h of heating, the reaction mixture was cooled down to room temperature over 2 h. Dark red crystals of 1 (1.9 mg, 1.4 µmol) were isolated in 33% yield. The PXRD pattern, thermogravimetric analysis plot, FT-IR spectrum, and $^{13}$C CP-MAS NMR spectrum are shown in Figures S2, S5, S6, and 2, respectively. The composition of 1 was determined based on a combination of elemental analysis, $^1$H NMR spectroscopy, and mass spectrometry. $^1$H NMR spectroscopy and mass spectrometry were performed on the digested sample of 1 (destroyed in the presence of HCl, Figure 2). PXRD was utilized to confirm crystallinity of the prepared material (Figure S2). Structural analysis was performed using the PXRD pattern of 1 in combination with the single-crystal data for Zn$_2$(ZnTCPP)(DPNI) (or PPF-18, [2] DPNI = N,N’-di-(4-pyridyl)-1,4,5,8-naphthalenetetracarboxydiimide) and the single-crystal data collected for the BPCF ligand, molecular complex, Ag$_2$(BPCF)$_2$(PF$_6$)$_2$, and two-dimensional network, Ag(BPCF)$_2$(PF$_6$) (Figure 1 and Figure S2). As a starting point for our simulation, we utilized the coordinates of the two dimensional porphyrin-based layers in the Zn$_2$(ZnTCPP)(DPNI) structure, and the size of the BPCF linker. The linker size was determined in the present work based on single-crystal X-ray analysis of the BPCF linker and its silver-containing compounds, molecular complex, Ag$_2$(BPCF)$_2$(PF$_6$)$_2$, and 2D network, Ag(BPCF)$_2$(PF$_6$) (Figures 1 and S1). The rationale behind the choice of the Zn$_2$(ZnTCPP)(DPNI) as a starting point for the structural analysis of 1 was based on the fact that the length of DPNI and BPCF pillars are comparable (15.5 Å for DPNI$^{[2]}$ and 15.8 Å for BPCF). As a result, the
PXRD pattern of as-synthesized 1 is consistent with the simulated pattern (Figure S2). For comprehensive analysis of 1, a combination of the solid-state $^{13}$C CP-MAS NMR and FT-IR spectroscopies was also utilized. Those spectroscopic studies have also confirmed coordinative immobilization of both porphyrin- and fullerene-based linkers in prepared 1 (Figures 2 and S6).

**Fluorescence Spectroscopy.** Emission spectra were acquired on an Edinburgh FS5 fluorescence spectrometer equipped with a 150 W Continuous Wave Xenon Lamp source for excitation. Emission measurements on solid samples were collected on the powders of the appropriate materials placed inside a 0.5 mm quartz sample holder using the front-facing module. Fluorescence quantum yield was measured using the integrating sphere module.

An emission response was also obtained using an Ocean Optics JAZ spectrometer. In this case, a mounted high-power 365 nm LED (M365L2, Thorlabs) was used as an excitation source.

Fluorescence lifetimes were measured using a Mini-$\tau$ lifetime spectrometer from Edinburgh Instruments equipped with a 365-nm picosecond-pulsed light-emitting diode (EPELED 365).

**Fitting of Fluorescence Decays.**

The fluorescence decays for 1 and Zn$_2$(ZnTCPP) shown in Figure S7 were fit with the triexponential function ($n = 3$):

$$I(t) = \int_0^t IRF(t') (C + \sum_{i=1}^{n} (B_i e^{-t'/\tau_i}) ) dt'$$

where $\tau_i$ and $B_i$ are respective lifetimes and amplitudes of each component.

The amplitude-weighted average fluorescence lifetimes were calculated based on the following equation:

$$\langle \tau_{aw} \rangle = \frac{B_1\tau_1 + B_2\tau_2 + B_3\tau_3}{B_1 + B_2 + B_3}$$

*eq. S2*
Table S1. Fluorescence decay lifetimes for 1 and Zn₂(ZnTCPP).

|          | B₁ | τ₁, ns | B₂ | τ₂, ns | B₃ | τ₃, ns | <τᵢ>₁, ns |
|----------|----|--------|----|--------|----|--------|-----------|
| Zn₂(ZnTCPP) | 0.23 | 0.32 | 0.76 | 1.29 | 0.00 | 4.20 | 1.07 |
| 1        | 0.69 | 0.31 | 0.31 | 1.01 | 0.00 | 7.08 | 0.54 |

**Energy transfer efficiency, Φₑₑ. Spectral overlap function, J. Förster radius, Rₒ.**

To calculate the energy transfer efficiency, the following equation was used:

\[
Φₑₑ = \frac{kₑ}{(kₒ + kₑ)}
\]

\[eq. S3\]

where \(k_r, k_{nr},\) and \(k_e = \) radiative decay, non-radiative decay, and energy transfer rate constants, respectively. Lifetime was used to find \(k_o\) and \(k_e\) values from the donor in the absence (\(\tau_D\)) and presence (\(\tau_{D,A}\)) of the acceptor, which are \(\tau_D = 1/k_o\) and \(\tau_{D,A} = 1/(k_o + k_e)\), respectively. The energy transfer efficiency was found to be 50%.

The following equation was used to calculate the spectral overlap function (\(J\)) from the experimental donor emission and acceptor absorption:

\[
J = \int f(λ)dλ, f(λ) = F(λ)ε(λ) λ^4
\]

\[eq. S4\]

where \(F(λ)\) is the donor emission spectrum normalized to unit area and \(ε(λ)\) is the molar extinction spectrum of the acceptor (Figure S8). The calculated overlap function was used to estimate the corresponding Förster critical radius (\(Rₒ\), the distance at which \(Φₑₑ\) is 50%): \n
\[
Rₒ (cm) = \left(8.79 \times 10^{-25} \times κ^2 n^{-4} Q_d\right)^{1/6}
\]

\[eq. S5\]

where \(Q_d = k_r \times \tau_D\) (\(k_r\) = donor radiative decay rate constant), \(κ\) is an orientation factor, and \(n\) is the refractive index (Figure S8).

**¹³C CP-MAS NMR Spectroscopy.** Solid-state NMR spectra (¹³C CP-MAS) were collected on a Bruker Avance III-HD 500 MHz spectrometer fitted with a 1.9 mm MAS probe. ¹³C{¹H} CP-MAS NMR spectra (125.79 MHz) were collected at ambient temperature with a sample rotation rate of 20 kHz. For cross polarization, 1.5 ms contact time with linear ramping on the ¹H channel and 62.5 kHz field on the ¹³C channel were used. ¹H dipolar decoupling was performed with
SPINAL64 modulation and 147 kHz field strength. Free induction decays (512–2048 transients) were collected with a 27 ms acquisition time over a 300 ppm spectrum width with a relaxation delay of 2.0 s. Data was processed after appropriate shifting of the echoes using Bruker Topspin 3.2.

**X-ray Crystal Structure Determination.**

**Single-crystal X-ray structure of C$_{75}$H$_{12}$N$_{2}$O$_{4}$ (BPCF).** Crystals of the compound grew as dark clusters composed of many intergrown flat needles. All larger crystals examined were multiply twinned. Eventually a single-domain specimen was located, which was reddish-brown in color. Single crystals are exceedingly thin, ca. 0.01 mm and the diffraction intensity is correspondingly weak. A scan time of 90 s per 0.5° frame was used for data collection. Despite this, no intensity was observed at higher angles. The dataset was truncated at 2θ$_{\text{max}}$ = 40.4° (d = 1.03 Å) at which point the mean I/σ(I) of the reflection data fell below 2.0. Data was collected at 100(2) K using a Bruker D8 QUEST diffractometer equipped with a PHOTON 100 CMOS area detector and an Incoatec microfocus source (Mo K$_{\alpha}$ radiation, λ = 0.71073 Å). The raw area detector data frames were reduced and corrected for absorption effects using the SAINT+ and SADABS programs. Final unit cell parameters were determined by least-squares refinement of 3792 reflections taken from the data set. The structure was solved by direct methods with SHELXT. Subsequent difference Fourier calculations and full-matrix least-squares refinement against $F^2$ were performed with SHELXL-2014 using OLEX2. The compound crystallizes in the orthorhombic system. The pattern of systematic absences in the intensity data was uniquely consistent with the space group $Pbc\alpha$. The asymmetric unit consists of one C$_{75}$H$_{12}$N$_{2}$O$_{4}$ molecule and an essentially continuous one-dimensional ribbon of disordered electron density running along the crystallographic $b$ axis and centered near $x,z = 1/4,1/4$ and symmetry-equivalent locations. Carbonyl oxygen O3 of the C$_{75}$H$_{12}$N$_{2}$O$_{4}$ molecule is disordered equally over two positions and were refined with half-occupancy. Their displacement parameters were held equal and additionally restrained to approximate a spherical shape (SHELX ISOR). A rigid-bond restraint (SHELX RIGU instruction) was applied to all atoms of the C$_{60}$ cage, to prevent some displacement ellipsoids from becoming unrealistically flattened (three became 'non-positive definite') along the cage
surface. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in geometrically idealized positions and included as riding atoms. The disordered interstitial species could not be modeled reasonably, and their contribution to the structure factors was accounted for during refinement using the Squeeze program.\cite{6,7} Squeeze calculated the volume occupied by these atoms to be 1382 Å$^3$, and they were calculated to contribute 332 electrons per unit cell to the scattering. This value corresponds to ca. 6.6 toluene molecules per cell, or 0.83 per C$_{72}$H$_{12}$N$_2$O$_4$ molecule. The final reported $F_{W\text{.}}, d$ (calc) and $F(000)$ refer to known species only. The largest residual electron density peak in the final difference map is 0.43 e$^-$/Å$^3$, located 1.53 Å from C2. The refinement data is given in Table S2.

**Single-crystal X-ray structure of Ag$_2$\(\text{(C}_{75}\text{H}_{12}\text{N}_{2}\text{O}_{4})_{2}\text{(PF}_{6}\text{)}_{2}\cdot\text{10(C}_{6}\text{H}_{6})\text{\text{(Ag}}_{2}\text{(BPCF)}_{2}\text{(PF}_{6}\text{)}_{2}\text{)).**

The compound crystallized as aggregations of thin brown parallelogram-shaped plates, with visually evident lamellar (plate-upon-plate) twinning. Numerous crystals were screened, most of which produced broad diffraction peaks with multiple maxima. The best crystal had no obvious peak splitting or pronounced streaking in the area detector images. Autoindexing routines gave the reported triclinic unit cell, but also suggested a C-centered monoclinic cell with a fair figure of merit ($a = 13.2$ Å, $b = 67.2$ Å, $c = 10.0$ Å, $\beta = 130.8^\circ$, $\alpha, \gamma \sim 90.2^\circ$). The crystal was eventually determined to be a pseudo-merohedral twin emulating the apparent monoclinic symmetry in the latter stages of the refinement (see below). X-ray intensity data covering the full sphere of reciprocal space were collected at 100(2) K using a Bruker D8 QUEST diffractometer equipped with a PHOTON 100 CMOS area detector and an Incoatec microfocus source (Mo K$_\alpha$ radiation, $\lambda = 0.71073$ Å).\cite{3} One phi and three omega scans of width 0.5$^\circ$ and a scan time of 50 s per image were collected at a crystal-to-detector distance of 60 mm. The raw area detector data frames were reduced and corrected for absorption effects using the SAINT+ and SADABS programs.\cite{3} Final unit cell parameters were determined by least-squares refinement of 9962 reflections taken from the data set. The structure was solved by direct methods with SHELXS.\cite{4} Subsequent difference Fourier calculations and full-matrix least-squares refinement against $F^2$ were performed with SHELXL-2014\cite{4} using OLEX2.\cite{5}

The compound crystallizes in the triclinic system. The space group $P$-1 (No. 2) was confirmed by structure solution. The asymmetric unit consists of half of one Ag$_2$\(\text{(C}_{75}\text{H}_{12}\text{N}_{2}\text{O}_{4})_{2}\text{\text{\text{2+}}}}\) cation, which is located on a crystallographic inversion center, one PF$_6$\text{\text{\text{2-}}}\) anion and five benzene
molecules of crystallization. All non-hydrogen atoms were refined with anisotropic displacement parameters (ADPs), however a free and unrestrained refinement resulted in 10 carbon atoms adopting physically senseless (“non-positive definite”) displacement parameters. These atoms were located in the C$_{60}$ cage and in the pyridyl ligand arms. To maintain physically reasonable ADPs, an enhanced rigid bond restraint (SHELX RIGU) was applied to the $U_{ij}$ values of the ligand atoms. An additional spherical ISOR restraint was necessary for pyridyl ring atom C7. In total, 993 displacement parameter restraints were used. The reason for this is likely the moderate crystallinity and twinning of the available samples. Hydrogen atoms bonded to carbon were located in Fourier difference maps before being placed in geometrically idealized positions included as riding atoms with $d$(C-H) = 0.95 Å and $U_{iso}$(H) = 1.2$U_{eq}$(C) for arene hydrogen atoms and $d$(C-H) = 0.99 Å and $U_{iso}$(H) = 1.2$U_{eq}$(C) for methylene hydrogens. The pseudo-merohedral twin law emulating the apparent monoclinic symmetry ($R_{int}$, monoclinic C = 0.18) was derived using the TwinRotMat program in PLATON.[7] The twin law is (-1 0 0 / 0 -1 0 / 1 1 1), corresponding to a 180° rotation perpendicular to the (001) plane. The refined major twin component volume fraction refined to 0.623(2). The largest residual electron density peak in the final difference map is 1.61 e-/Å$^3$, located 1.09 Å from Ag1, and is not chemically significant.

**Single-crystal X-ray structure of Ag(C$_{75}$H$_{12}$N$_{2}$O$_{4}$)$_{2}$][PF$_{6}$]·5(C$_{6}$H$_{6}$) (Ag(BPCF)$_{2}$(PF$_{6}$)).** X-ray intensity data from a dark brown tablet were collected at 100(2) K using a Bruker D8 QUEST diffractometer equipped with a PHOTON 100 CMOS area detector and an Incoatec 'high-brilliance' microfocus source (Mo K$_{a}$ radiation, $\lambda$ = 0.71073 Å).[3] The raw area detector data frames were reduced and corrected for absorption effects using the SAINT+ and SADABS programs.[3] Final unit cell parameters were determined by least-squares refinement of 9354 reflections taken from the dataset. The structure was solved by direct methods with SHELXS.[4] Subsequent difference Fourier calculations and full-matrix least-squares refinement against $F^2$ were performed with SHELXL-2014[4] using OLEX2.[5]

The compound crystallizes in the monoclinic system. The pattern of systematic absences in the intensity data was consistent with the space group $P2_1/c$, which was confirmed by structure solution. The asymmetric unit consists of one silver atom, one PF$_{6}^-$ anion, two independent C$_{75}$H$_{12}$N$_{2}$O$_{4}$ ligands, four complete benzene molecules and half each of two additional benzene molecules located on crystallographic inversion centers. Refinement precision was limited by disorder of one C$_{60}$ cage and three -CC(O)OCH$_{2}$C$_{5}$H$_{4}$N arms from the two independent
C$_{75}$H$_{12}$N$_2$O$_4$ ligands. Further, a pattern of small residual electron density peaks (< 0.5 e-/Å$^3$) among atoms of the other C$_{60}$ cage (C101–C160) suggests minor disorder of this cage also, but a stable disorder model could not be attained because of the apparent low disorder faction (trial occupancies $<< 10\%$). The disordered C$_{60}$ cage was refined with two independent orientations, C201–C260 and C301–C360. Both were restrained to be geometrically similar to the ordered C$_{60}$ ball (C101–C160) using SHELX SAME instructions. The disorder extends into both ligand arms attached to this cage. These were also modeled with two orientations (C16–C17, O5 A/B and C24–C30, O7, O8, N2 A/B). The major disorder fraction of this ligand refined to 0.638(3). Disorder of ligand arm C9–C15, N2, O3, O4 was also modeled with two components A/B with a major group occupancy of 0.626(6). Appropriate 1,2- and 1,3- distance restraints were applied to atom pairs of the ligand arms. Displacement parameters for nearly superimposed atoms were held equal. Most non-hydrogen atoms were refined with anisotropic displacement parameters, the exception being disordered benzene molecules with fractional occupancies $\leq 0.5$, which were refined isotropically. Enhanced rigid-bond (RIGU) restraints were applied to the ligand arm and disordered C$_{60}$ atoms (C201–C260 and C301–C360) atoms to maintain physically reasonable anisotropic displacement parameters. Benzene molecules C421–C426 and C451-C453 were restrained to adopt a similar geometry as the best-behaved benzene C401–C406. Disordered and partially occupied benzene molecules C441-C446 and C421-C426/C521-C526 were refined as rigid hexagons. Hydrogen atoms placed in geometrically idealized positions included as riding atoms with $d$(C-H) = 0.95 Å and $U_{iso}$(H) = 1.2$U_{eq}$(C) for benzene and pyridyl ring hydrogen atoms and $d$(C-H) = 0.99 Å and $U_{iso}$(H) = 1.2$U_{eq}$(C) for methylene hydrogens. The largest residual electron density peak in the final difference map is 0.73 e-/Å$^3$, located 1.43 Å from C453. This suggests further minor disorder of this group, though trial modeling efforts were not stable and did not improve the refinement.

**Computational Details.** Several DFT computational codes were employed to solve different tasks. Optimization of the molecular and periodic structures was performed at PBE/DZVP level of theory using CP2K code$^{[8-11]}$ with $\Gamma$-point approximation for the solid state. Single point band structure calculations were performed at the PBE/DZ level of theory with the GPAW code.$^{[11-13]}$ The electron density was converged with k-mesh 4×4×1 for Zn$_2$(ZnTCPP) and 2×2×1 for 1. The Harris calculation for the bands was performed with a resolution of 100 grid-points along X-Y-Z.
Γ-X lines, implying the orthorhombic cell with $a = b$ parameters. Time-dependent DFT calculations were performed using long-range corrected CAM-B3LYP functional and DZVP-quality basis set implemented in the GAMESS-US code.\cite{14,15} The CAM-B3LYP is known to have much better reliability in prediction of CT excitations. In TD-DFT calculations, only a fragment comprising BPCF linked to ZnTCPP was used (Figure 3). More computational details are shown below.

**Other Physical Measurements.** FT-IR spectra were obtained on a Perkin-Elmer Spectrum 100. NMR spectra were collected on Bruker Avance III-HD 300 and Bruker Avance III 400 MHz NMR spectrometers. $^{13}$C and $^1$H NMR spectra were referenced to natural abundance $^{13}$C peaks and residual $^1$H peaks of deuterated solvents, respectively. Powder X-ray diffraction patterns were recorded on a Rigaku Miniflex II diffractometer with accelerating voltage and current of 30 kV and 15 mA, respectively. Thermogravimetric analysis was performed on an SDT Q600 Thermogravimetric Analyzer using an alumina boat as a sample holder. The Waters QTOF-I quadrupole time-of-flight mass spectrometer was used to record the mass spectra of the prepared compounds. Diffuse reflectance spectra were collected on a Perkin Elmer Lambda 45 UV-vis spectrometer referenced to Spectralon®.
**Figure S1.** *(top-left)* The molecular structure of the BPCF ligand. The displacement ellipsoids are drawn at the 50% probability level. *(top-right)* The single-crystal structure of the Ag₂(BPCF)₂(PF₆)₂ molecular complex. The displacement ellipsoids are drawn at the 60% probability level. *(bottom)* The single-crystal structure of the two-dimensional Ag(C₇₅H₁₂N₂O₄)₂(PF₆) network, the displacement ellipsoids are drawn at the 40% probability level. The solvent molecules (benzene) and PF₆⁻ anions are omitted for clarity. Dark blue, light blue, red, gray, and white spheres represent Ag, N, O, C, and H atoms, respectively.
Figure S2. The experimental and simulated (in the 110 preferential orientation) PXRD patterns of 1 and Zn₂(ZnTCPP)(DPNI),[2] respectively. The inset shows the unit cell parameters of two-dimensional Zn₂(ZnTCPP)[16] (left) and simulated 1 (right).
Figure S3. The crystal structure of two-dimensional Zn₂(ZnTCP).\textsuperscript{[16]} The inset shows a Zn₂(O₂C–)₄ secondary building unit (SBU). The green spheres highlight the apical positions of the SBUs occupied by the solvent molecules. Orange, red, and gray spheres represent Zn, O, and C atoms, respectively. The solvent molecules and hydrogen atoms are omitted for clarity.
Figure S4. A schematic representation of BPCF installation between two-dimensional Zn₂(ZnTCPP)\textsuperscript{[16]} layers.
**Figure S5.** Thermogravimetric analysis plot of as-synthesized 1.
Figure S6. The FT-IR spectra of BPCF (blue), 1 (black), and Zn$_2$(ZnTCPP) (red).
Figure S7. Fluorescence decays of 1 (green) and Zn$_2$(ZnTCPP) (red). Black solid lines are fits of the decays, according to eq. S1.
Figure S8. Förster analysis of 1, which illustrates an overlap of BPCF acceptor and Zn$_2$(ZnTCPP) donor. The overlap function (dashed line, left vertical axis) versus wavelength, $\lambda$, is given by $f(\lambda) = F(\lambda)\varepsilon(\lambda)\lambda^4$ with $F(\lambda)$, the donor emission spectrum, normalized to unit area (green line, arbitrary scale), $\varepsilon(\lambda)$ is the molar extinction spectrum of BPCF (red line, right vertical axis) in CS$_2$. The spectral overlap integral, $J = \int f(\lambda)d(\lambda)$, controls the energy transfer rate $k_{ET}$. The spectral overlap integral was found to be $2.34 \times 10^{-15}$ cm$^3$ M$^{-1}$. $R_o$ was estimated to be 19 Å.
Table S2. X-ray structure refinement data for BPCF<sup>a</sup> and Ag<sub>2</sub>(BPCF)<sub>2</sub>(PF<sub>6</sub>)<sub>2</sub> <sup>a</sup>.

| Compound                  | BPCF                  | Ag<sub>2</sub>(BPCF)<sub>2</sub>(PF<sub>6</sub>)<sub>2</sub> | Ag(C<sub>75</sub>H<sub>12</sub>N<sub>2</sub>O<sub>4</sub>)<sub>2</sub>(PF<sub>6</sub>)<sub>2</sub> |
|---------------------------|-----------------------|----------------------------------------------------------|----------------------------------------------------------|
| **Formula**               | C<sub>75</sub>H<sub>12</sub>N<sub>2</sub>O<sub>4</sub> | C<sub>210</sub>H<sub>84</sub>Ag<sub>2</sub>F<sub>12</sub>N<sub>4</sub>O<sub>8</sub>P<sub>2</sub> | C<sub>180</sub>H<sub>54</sub>AgF<sub>6</sub>N<sub>4</sub>O<sub>8</sub>P<sub>2</sub> |
| **FW**                    | 1004.87               | 3296.49                                                  | 2653.11                                                  |
| **T, K**                  | 100(2)                | 100(2)                                                   | 100(2)                                                   |
| **Crystal System**        | orthorhombic          | triclinic                                                | monoclinic                                               |
| **Space Group**           | Pbca                  | P-1                                                      | P2<sub>1</sub>/c                                         |
| **Z**                     | 8                     | 1                                                        | 4                                                        |
| **a, Å**                  | 20.741(2)             | 9.9693(17)                                               | 27.5312(16)                                             |
| **b, Å**                  | 9.8500(11)            | 10.037(17)                                               | 20.3038(11)                                             |
| **c, Å**                  | 42.484(4)             | 34.229(6)                                                | 20.0238(12)                                             |
| **α, °**                  | 90                    | 97.239(4)                                                | 90                                                      |
| **β, °**                  | 90                    | 96.966(4)                                                | 102.7850(15)                                            |
| **γ, °**                  | 90                    | 98.030(4)                                                | 90                                                      |
| **V, Å<sup>3</sup>**      | 8679.6(16)            | 3330.7(10)                                               | 10915.6(11)                                             |
| **d<sub>calc</sub>, g/cm<sup>3</sup>** | 1.538                | 1.643                                                   | 1.614                                                   |
| **µ, mm<sup>-1</sup>**    | 0.096                 | 0.413                                                   | 0.290                                                   |
| **F(000)**                | 4064.0                | 1668.0                                                   | 5367.0                                                  |
| **Crystal Size/mm<sup>3</sup>** | 0.26 × 0.04 × 0.01   | 0.44 × 0.12 × 0.02                                       | 0.2 × 0.2 × 0.05                                         |
| **θ Range**               | 4.308 to 40.36        | 4.482 to 50.146                                          | 4.172 to 50.192                                         |
| **Index Ranges**          | -20 ≤ h ≤ 20          | -11 ≤ h ≤ 11                                             | -32 ≤ h ≤ 32                                            |
|                           | -9 ≤ k ≤ 9            | -11 ≤ k ≤ 11                                             | -24 ≤ k ≤ 24                                            |
|                           | -41 ≤ l ≤ 41          | -40 ≤ l ≤ 40                                             | -23 ≤ l ≤ 23                                            |
| **Reflected Collected**   | 59842                 | 44251                                                    | 259533                                                  |
| **Data/Restraints/Parameters** | 4155/825/734          | 11494/993/1073                                          | 19385/3030/2414                                         |
| **GOF on F<sup>2</sup>**  | 1.086                 | 1.041                                                   | 1.115                                                   |
| **Largest Peak/Hole, e/Å<sup>3</sup>** | 0.43/-0.32         | 1.61/-1.64                                              | 0.72/-1.23                                             |
| **R<sub>1</sub> (wR<sub>2</sub>)**, % | 7.96 (19.10)         | 8.62 (19.18)                                             | 7.13 (14.14)                                            |

<sup>a</sup> Mo-Kα (λ = 0.71073 Å) radiation

<sup>b</sup> R<sub>1</sub> = Σ||F<sub>o</sub>| - |F<sub>c</sub|| / Σ |F<sub>o</sub|, wR<sub>2</sub> = [Σ [w(F<sub>o</sub> - F<sub>c</sub>)<sup>2</sup>]/ Σ [w(F<sub>o</sub>)<sup>2</sup>]<sup>1/2</sup>
**Discussion of computational results.** The structures of Zn$_2$(ZnTCPP) and 1 were optimized assuming a square lattice ($a = b$) with different lattice parameters. Figure S9 shows the total energy as a function of the $a$ parameter. The lowest energies are found near the $a$ values of 16.7 and 16.8 Å, reasonably close to the experimental values.

![Figure S9. Potential energy profile as a function of the unit cell parameter for Zn$_2$(ZnTCPP) (right) and 1 (left).](image)
Band structure of Zn$_2$(ZnTCPP) and 1. Band structure calculations show that the bands of both systems near the Fermi level are flat, which means that they can be treated as localized systems.

Figure S10. Band structure of Zn$_2$(ZnTCPP) (left) and 1 (right) along the X-Y-Γ-X lines of the tetragonal lattice. Blue lines are valence bands, and green lines are conduction bands.
**Computations of Excitation Energies.** The localized nature of the frontier orbitals of 1 enables the use of a molecular fragment for the analysis of the possible excitation pathways. Therefore, we used a dyad comprising BPCF coordinating to ZnT CPP, BPCF–ZnT CPP (Figure 3), to model excited states of 1. Since prediction of charge-transfer excitations in the framework of TD-DFT approach is very problematic for standard DFT functional, a long-range corrected functional CAM-B3LYP was used.

Figure S11 shows a frontier MO energy diagram of the molecular dyad (Figure 3) and visualizes representative MOs. HOMO and HOMO-1 of this model are localized on the ZnT CPP moiety and resemble the two-fold degenerate HOMO of ZnT CPP. At lower energies follow 5 C₆₀-localized MOs resembling the 5-fold degenerate HOMO of C₆₀. LUMO, LUMO+1, and LUMO+2 of BPCF–ZnT CPP resemble the 3-fold degenerate LUMO of C₆₀, whereas LUMO+3 and LUMO+4 are similar to the 2-fold degenerate LUMO of ZnT CPP. In this model, three types of excitations may have comparable energies: excitations in the ZnT CPP moiety (denoted as ZnT CPP*), excitations in the BPCF moiety (denoted as BPCF*), and charge-transfer excitations between ZnT CPP-localized HOMOs and C₆₀-based LUMOs (denoted as CT). Difference densities for three types of excitations obtained in TD-DFT calculations are shown on Figure S12.

**Figure S11.** Energies and representative isosurfaces of the frontier molecular orbitals of the BPCF–ZnT CPP molecular dyad. Red arrows show three types of excitations expected in this system (Note that these are formal directions; both BPCF* and CT states can be achieved via excitation of the ZnT CPP moiety with subsequent energy or charge transfer to the BPCF).
Figure S12. Difference density for three types of excitations in the BPCF-ZnTCPP dyad.
Table S3. Excitation energies (eV) of the BPCF-ZnTCPP dyad.

| #  | "raw"  | f    | type    |
|----|--------|------|---------|
| 1  | 2.168  | 0.004| ZnTCPP* |
| 2  | 2.193  | 0.004| ZnTCPP* |
| 3  | 2.368  | 0.001| BPCF*   |
| 4  | 2.382  | 0    | BPCF*   |
| 5  | 2.463  | 0    | BPCF*   |
| 6  | 2.487  | 0    | BPCF*   |
| 7  | 2.526  | 0    | CT      |
| 8  | 2.578  | 0    | BPCF*   |
| 9  | 2.629  | 0    | CT      |
| 10 | 2.658  | 0    | CT      |

Table S3 lists computed excitation energies for the BPCF-ZnTCPP model, whereas Table S4 compares computed and experimental excitation energies of the BPCF and ZnTCPP. Surprisingly, TD-DFT predicts that the two lowest-energy transitions have ZnTCPP* character followed by a manifold of BPCF* and CT excitations with similar energies. Thus, BPCF* and CT states have similar energies and both states can be considered as similarly probable, as long as their energetics is concerned. Table S4 compares computed excitation energies of ZnTCPP and BPCF molecules with experimental data (experimental $S_1$ energies for ZnTCPP and BPCF are 2.03 and 1.73 eV, respectively). Based on the obtained results, CAM-B3LYP overestimated Q-type excitation energy of ZnTCPP by 0.26 eV and the $S_1$ energy of BPCF by 0.76 eV (notably, the Soret-type excitation, overestimation is similar to that of $C_{60}$). Since excitations in the BPCF-ZnTCPP model are almost localized on the fragments, it is reasonable to expect similar errors for ZnTCPP and BPCF-based excitations. If these systematic errors are taken into account, ZnTCPP* and BPCF* energies in the dyad should be reverted, i.e. BPCF* excitation energies are expected to be lower than ZnTCPP*. 
Table S4. Excitation energies (eV) of BPCF and ZnTCPP.

|        | calc | f   | exp |
|--------|------|-----|-----|
| **BPCF**<br>1 | 2.493 | 0.002 | 1.73 |
| 2 | 2.520 | 0.000 |
| 3 | 2.587 | 0.000 |
| 4 | 2.608 | 0.000 |
| **ZnTCPP**<br>1 | 2.286 | 0.002 | 2.03 | Q-type |
| 2 | 2.286 | 0.002 | |
| 3 | 3.443 | 1.652 | 2.87 | Soret |
| 4 | 3.445 | 1.656 | |
Figure S13. The FT-IR spectra of BPCF (black) and the Ag$_2$(BPCF)$_2$(PF$_6$)$_2$ molecular complex (blue).
Figure S14. The FT-IR spectra of BPCF (black) and the two-dimensional Ag(BPCF)_2(PF_6) network (blue).
Figure S15. The simulated (black) and experimental (blue) PXRD patterns of Ag(BPCF)$_2$(PF$_6$).
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