

Metal–Organic Frameworks

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

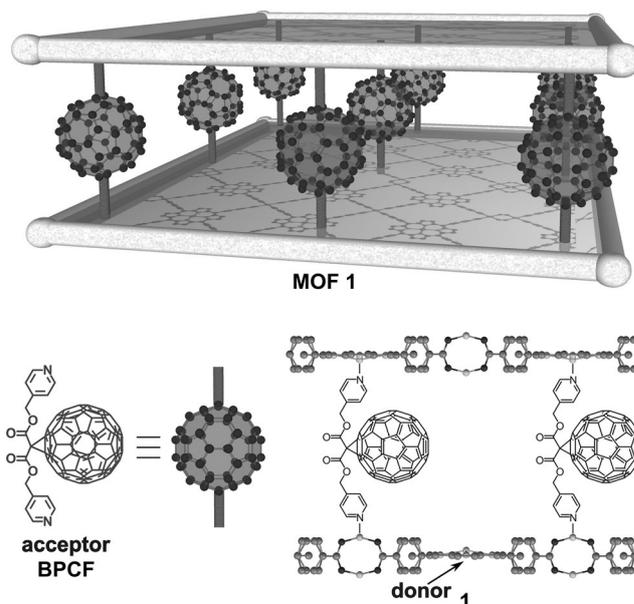
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Abstract: Herein, we report the first example of a crystalline metal–donor–fullerene framework, in which control of the donor–fullerene mutual orientation was achieved through chemical bond formation, in particular, by metal coordination. The ^{13}C cross-polarization magic-angle spinning NMR spectroscopy, X-ray diffraction, and time-resolved fluorescence spectroscopy were performed for comprehensive structural analysis and energy-transfer (ET) studies of the fulleretic donor–acceptor scaffold. Furthermore, in combination with photoluminescence measurements, the theoretical calculations of the spectral overlap function, Förster radius, excitation energies, and band structure were employed to elucidate the photophysical and ET processes in the prepared fulleretic material. We envision that the well-defined fulleretic donor–acceptor materials could contribute not only to the basic science of fullerene chemistry but would also be used towards effective development of organic photovoltaics and molecular electronics.

The success of fullerenes and their derivatives in engineering organic photovoltaics and molecular electronics is mainly owed to their electron-accepting properties and ultrafast electron/energy transfer.^[1,2] As previously demonstrated, fullerene(acceptor)–donor alignment could significantly affect excitonic device performance. For instance, the arrangement of the donor fullerene is crucial for efficient energy/charge transfer, because of possible effects on the distance of exciton diffusion, π – π stacking, or Förster radius (resonance energy transfer). As a result, formation of full-

erene stacks led to an enhancement of solar cell efficiency, in contrast to non-stacking fullerene derivatives.^[3]

There are few known reports of spatial organization of graphitic crystalline materials through the covalent linkage of fullerene derivatives.^[4–8] Moreover, the known approaches for fulleretic material organization are mainly based on immobilization of the fullerenes inside porous matrices possessing a large aperture.^[9–11] There are very few reports of crystalline fullerene–metal-coordinated extended structures.^[12–15] Furthermore, none of these studies explore the concept demonstrated herein, which tackles the development of a novel crystalline metal–donor–acceptor framework, in which control of the mutual orientation of the donor and fullerene-based acceptor was achieved through chemical bond formation, that is, metal coordination. Despite the tremendous interest in self-assemblies (in particular, coordination polymers such as covalent or metal–organic frameworks; COFs or MOFs)^[16–30] and fullerene chemistry, to the best of our knowledge the prepared metal–organic fullerene-containing framework is the first example of a crystalline hybrid-extended structure, in which control over mutual orientation of both donor and fullerene-based acceptor is achieved through metal coordination (Scheme 1).



Scheme 1. A schematic representation of organization of porphyrin-based donors and fullerene-based electron-accepting linkers in the crystalline network **1** through metal coordination.

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To study the photophysical properties and energy-transfer processes (i.e., key components for development of any photonic device), and perform a comprehensive analysis of the donor–acceptor MOF, ^{13}C cross-polarization magic-angle spinning (CP-MAS) solid-state NMR spectroscopy, powder X-ray diffraction, and time-resolved fluorescence spectroscopy were employed. Furthermore, combination of photoluminescence measurements with theoretical calculations of the spectral overlap function, Förster radius, excitation energies, scaffold potential-energy profile, and band structure were used to shed light on the photophysical processes occurring between porphyrin-based donor and fullerene-containing electron-accepting linkers.

The possibility of dense carbon-cage decoration makes fullerene chemistry very rich, but, at the same time, imposes a challenge to control the number of addends and, as a result, isolate fullerene derivatives with the desired number of groups. For instance, multiple additions to a fullerene cage in a one-pot reaction could result in a high degree of fullerene derivatization. Indeed, there are fullerene-based compounds which contain 18, 20, or even more than 40 groups on the carbon cage.^[31,32] Furthermore, fullerene derivatives with a close number of addends (e.g., 10, 12, or 14) or the same number of groups but with different addition patterns (i.e., different position of the groups on the carbon sphere) possess very similar physicochemical properties, which also impede their separation.^[33,34] As a result, the vast majority of fullerene derivatives are typically isolated on a milligram-scale by use of labor-intensive high-performance liquid chromatography (HPLC). These facts result in a significant challenge for the synthesis of fullerene-containing linkers in quantities not only sufficient for material preparation but also comprehensive characterization for further photophysical studies of the hybrid donor–fullerene frameworks.

For this reason, the presented studies focus on material development, which involves the synthesis of fullerene-containing ligands accessible on a gram scale without use of the demanding HPLC technique. As a result, we have chosen to derivatize the carbon sphere with two pyridyl arms and prepared bis(pyridin-4-ylmethyl)-3'-H-cyclopropa-[1,2](C₆₀-I_h)[5,6]fullerene-3',3'-dicarboxylate (BPCF), for which purification was accomplished without HPLC (more experimental details can be found in the Supporting Information). The single crystals of BPCF, Ag₂(BPCF)₂(PF₆)₂, and two-dimensional Ag(BPCF)₂(PF₆) necessary for the structural analysis of the prepared hybrid materials (for more details see the Supporting Information), were grown from saturated toluene, methanol/benzonitrile/benzene and acetonitrile/benzene solutions, respectively. Figure 1 shows the structures and packing of BPCF, Ag₂(BPCF)₂(PF₆)₂, and Ag(BPCF)₂(PF₆).

For self-assembly of the donor–acceptor framework, porphyrin-containing ligands were chosen as donors because of their (i) typically large absorption coefficients in the visible region, (ii) rigid molecular structures necessary for the chosen synthetic strategy, (iii) behavior as molecular tweezers towards fullerene-containing compounds,^[35] and iv) facile charge/energy transfer previously observed in molecular fullerene–porphyrin ensembles.^[36]

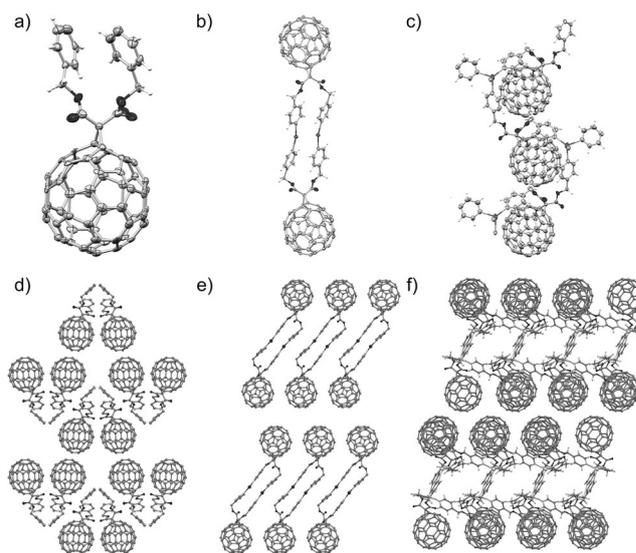


Figure 1. The single-crystal X-ray structures and crystal packing of BPCF (a,d), Ag₂(BPCF)₂(PF₆)₂ (b,e), and Ag(BPCF)₂(PF₆) (c,f). Displacement ellipsoids drawn at the 50% probability level for BPCF, 60% for Ag₂(BPCF)₂(PF₆)₂, and 40% for Ag(BPCF)₂(PF₆).

To engineer the proposed donor–fullerene crystalline hybrids, we have applied a synthetic procedure, which is based on organization of porphyrin-based donors in two-dimensional layers, followed by the installation of the fullerene-based ligands between them (Scheme 1 and Figure S4). As previously shown, reactions of tetrakis(4-carboxyphenyl)porphyrin (H₄TCPP) linkers with metal salts (in the absence of BPCF) led to the formation of two-dimensional planar Zn₂(ZnTCPP) layers, in which the porphyrin-containing donors were connected through Zn₂(O₂C-) secondary building units (SBUs).^[37] Figure S3 shows that the solvent molecules occupy the apical positions of the Zn₂(O₂C-) SBUs and could be replaced by different linkers which connect two adjacent Zn₂(ZnTCPP) layers (Figure S4). Thus, Zn²⁺ ions in Zn₂(O₂C-) could be used as anchor points for arrangement of the fullerene-based acceptors by coordinative immobilization between the layers. To prepare such a fullerene–porphyrin crystalline hybrid framework, H₄TCPP and BPCF were heated in the presence of zinc nitrate at 80 °C for 16 h, which resulted in formation of [Zn₂(ZnTCPP)(BPCF)_{0.23}(DEF)_{0.77}·2(EtOH)·0.2H₂O (**1**, Scheme 1; the synthetic details can be found in the Supporting Information). Interestingly, employment of the same synthetic scheme for incorporation of the parent fullerene C₆₀ (i.e., without pyridyl groups) within porphyrin layers was not successful.

Comprehensive analysis of synthesized **1** was performed by powder X-ray diffraction (PXRD), diffuse reflectance, infrared, and solid-state ^{13}C CP-MAS NMR spectroscopy, and elemental and thermogravimetric analyses. In addition, ^1H NMR spectroscopy and mass spectrometry were also employed to study the composition of digested **1** (decomposed in the presence of hydrochloric acid, Figure 2a,b). Structural analysis revealed that the interlayer distance, which is measured from the apically bound atom at the Zn₂(O₂C-) SBU to the apically bound atom at the metalated porphyrin

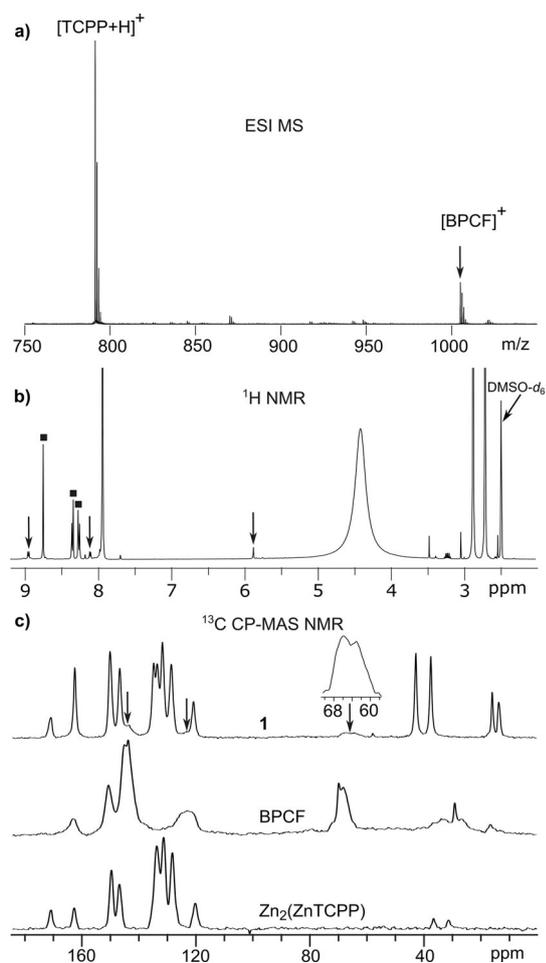


Figure 2. a) Electrospray ionization mass-spectrometry (ESI-MS) of digested **1**. b) The ^1H NMR spectrum of digested **1**. The resonances corresponding to H_4TCPP (\blacksquare) in the ^1H NMR spectrum are labeled. c) Solid-state ^{13}C CP-MAS NMR spectra of **1**, BPCF, and two-dimensional porphyrin-based framework, $\text{Zn}_2(\text{ZnTCPP})$. The arrows indicate BPCF.

center of the next layer, had expanded from 2.82 Å, observed for a 2D porphyrin-based framework without fullerene linkers,^[37] to 15.4 Å in **1** containing BPCF linkers, which is in line with the length of the pyridyl arms calculated from the single-crystal structure of BPCF (Figures 1 and S2; more details are given in the Supporting Information). Coordinative immobilization of both linkers inside the rigid donor-acceptor framework **1** was also confirmed based on a combination of ^{13}C CP-MAS and ^1H NMR spectroscopy and mass spectrometry (Figure 2). In Figure 2a, the mass-spectrum of digested **1** clearly indicates the presence of both porphyrin- and fullerene-based linkers. Both solution ^1H NMR and solid-state ^{13}C CP-MAS NMR spectroscopic data of digested and as-synthesized **1**, respectively, have also confirmed the successful immobilization of fullerene-based BPCF linkers inside the porphyrin-based matrix (Figure 2). Thus, to the best of our knowledge, we prepared the first example of a crystal-line covalently linked metal-donor-fullerene network.

Density functional theory (DFT) calculations at the PBE/DZVP level of theory were performed to obtain a deeper insight into the structural and electronic properties of **1**.^[38]

The Γ -point optimization (with CP2K code),^[39–41] assuming the tetragonal lattice ($a = b$), gives values of 16.7 and 16.8 Å, for $\text{Zn}_2(\text{ZnTCPP})$ framework and **1**, respectively. The inter-layer distance in **1** is predicted to be 19.4 Å, which is in good agreement with PXRD data.

Band-structure calculations for optimized structures (GPAW code)^[42,43] showed the bands near Fermi level are flat (i.e. have small dispersion), which indicates that the frontier orbitals have a localized nature. Figure 3a,b shows that the HOMO and LUMO of **1** in the Γ -point are localized on ZnTCPP and C_{60} moieties, respectively, similar to the molecular C_{60} -ZnTCPP dyads.^[44]

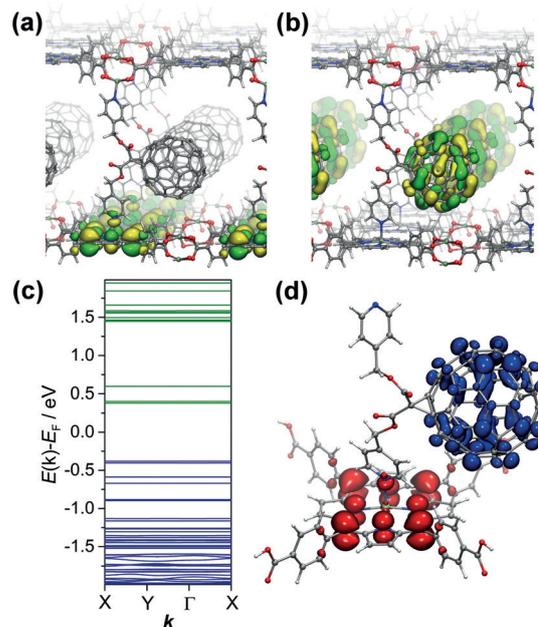


Figure 3. DFT-calculated HOMO (a) and LUMO (b) of **1** at the Γ point. c) Band structure of **1** calculated for the tetragonal lattice with $a = b$. d) Difference density for the charge-transfer excitation in the BPCF-ZnTCPP molecular dyad.

To study photophysical properties of **1**, photoluminescence (PL), diffuse reflectance, and time-resolved photoluminescence spectroscopic studies were employed. As clearly visible by the naked eye, immobilization of the fullerene-based linker, BPCF, resulted in significant quenching of the PL response in comparison with the two-dimensional $\text{Zn}_2(\text{ZnTCPP})$ framework containing exclusively porphyrin-containing donors (Figure 4). This fact is also in line with the performed time-resolved fluorescence studies. Indeed, analysis of the time-resolved PL decay curves with a reconvolution fit supported triexponential decays in each case, indicating a shortening of the amplitude-weighted average lifetime from 1.07 to 0.54 ns in 2D porphyrin-based MOF and **1**, respectively (see Equations S1 and S2 in the Supporting Information). Based on the decreased lifetime, the energy-transfer efficiency and estimated rate constant were found to be 49.5% and $9.18 \times 10^8 \text{ s}^{-1}$, respectively (more details can be found in the Supporting Information). The lifetime decrease observed in **1** could be explained by

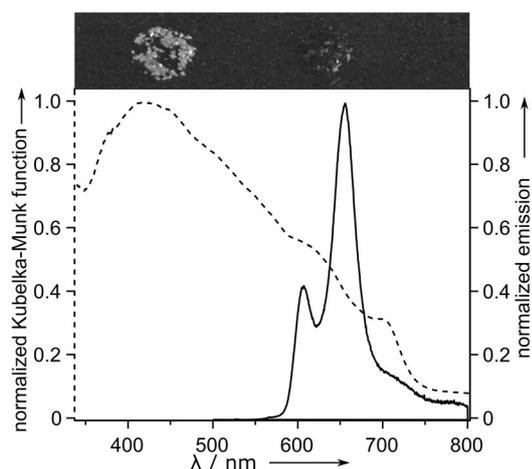


Figure 4. Normalized diffuse reflectance of BPCF (dashed line) and emission of the two-dimensional porphyrin-based framework Zn_2 -(ZnTCPP) (solid line). Photograph of Zn_2 (ZnTCPP) crystals (top left) and framework **1** (top right) under irradiation ($\lambda_{ex} = 365$ nm) using a high-power light-emitting diode.

activation of non-radiative pathways, among which Förster (or fluorescence) resonance energy transfer (FRET) is a commonly attributed pathway in a MOF matrix.^[45,46] FRET relies on the transfer of excitation energy in a non-radiative fashion through long-range dipole–dipole interactions, for which donor emission and acceptor absorption profiles must overlap. Indeed, Figure 4 demonstrates a significant overlap of Zn_2 (ZnTCPP) (donor) emission and BPCF (acceptor) absorption. To further explore the possibility of FRET in **1**, the Förster critical radius (R_0) was estimated through calculation of the spectral overlap function, J ($J = 2.34 \times 10^{-15} \text{ cm}^3 \text{ M}^{-1}$), between the donor and the acceptor (see the Supporting Information for more details). On the basis of the calculated J , we estimated R_0 to be 18.8 Å, which is beyond the donor–acceptor distance approximated from the structural data. It is important to note that ET was described as the most probable pathway in the fullerene–ZnTCPP dyads in nonpolar solvents.^[47] At the same time, while FRET could be responsible for observed emission quenching/lifetime decrease in **1**, charge transfer (CT), often observed for fullerene–porphyrin dyads in polar solvents^[48] could not be ruled out. Using the locality of the frontier molecular orbitals in **1**, we performed calculations of the excitations for the BPCF–ZnTCPP dyad as a truncated model of **1** comprised of one BPCF coordinated to ZnTCPP through its pyridyl arm (Figure 3). Time-dependent DFT calculations at the CAM-B3LYP/DZP level of theory (Gamess-US code)^[49,50] showed that the charge-transfer excitation (see Figure 3d for the difference density) has similar energy to that of C_{60} -based excitations. Thus, thermodynamics of FRET and CT processes are predicted to be comparable (see Supporting Information for more detailed discussion of TD-DFT calculations, see Figures S9–S12, Tables S3 and S4).

The forgoing results demonstrate a synthetic strategy for preparation of a donor–fullerene crystalline extended structure, in which precise orientation of the donor versus acceptor was achieved through metal coordination. In the course of

these studies, the single-crystal X-ray structure of fullerene-based acceptor, BPCF, was also determined. Time-resolved PL studies were utilized to estimate the spectral overlap function as well as ET efficiency in the prepared fullerene crystalline donor–acceptor material. Furthermore, the acquired PL data in combination with theoretical calculations (e.g., Förster radius, excitation energies, band structure, and spectral overlap function) were utilized to shed light on photophysics of the prepared fullerene donor–acceptor scaffold. Since organization of fullerene-based acceptors at the nanoscale level and their mutual orientation with the donor molecules is demanded by a variety of practical applications, we envision that these studies could contribute not only in the basic science of fullerene chemistry but also in the development of the next generation of organic photovoltaics and molecular electronics.

Experimental Section

Full experimental and computational details can be found in the Supporting Information. CCDC 1472926 (BPCF), 1472925 (Ag_2 -(BPCF)₂(PF₆)₂), and 1472927 (Ag (BPCF)₂(PF₆)), contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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