MIT Open Access Articles

Turn-on fluorescence in tetraphenylethylene-based metal-organic frameworks: An alternative to aggregation-induced emission

Turn-On Fluorescence in Tetraphenylethylene-Based Metal-Organic Frameworks: an Alternative to Aggregation-Induced Emission

Natalia B. Shustova, Brian D. McCarthy, and Mircea Dincă[*]

Department of Chemistry, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, MA, 02139

mdinca@mit.edu

Coordinative immobilization of functionalized tetraphenyl-ethylene within rigid porous metal-organic frameworks (MOFs) turns on fluorescence in the typically non-emissive tetraphenylethylene core. The matrix coordination-induced emission effect (MCIE) is complementary to aggregation-induced emission. Despite the large interchromophore distances imposed by coordination to metal ions, a carboxylate analogue of tetraphenylethylene anchored by Zn^{2+} and Cd^{2+} ions inside MOFs shows fluorescence lifetimes in line with those of close-packed molecular aggregates. Turn-on fluorescence by coordinative ligation in a porous matrix is a powerful approach that may lead to new materials made from chromophores with molecular rotors. The potential utility of MCIE towards building new sensing materials is demonstrated by tuning the fluorescence response of the porous MOFs as a function of adsorbed small analytes.

The immense interest in organic chromophores is driven by their utility towards the manufacture of cheap and efficient electronic devices such as photovoltaic cells and light-emitting diodes.[1] Often, the design of new chromophores relies on tuning the *molecular* electronic structure, yet it is the properties of molecular *aggregates* that ultimately dictate device performance. For instance, most molecular organic chromophores are highly emissive in solution but become non-emissive in the solid state due to aggregation-caused quenching.[2] Some chromophores, however, display the opposite effect: they show no emission in dilute solutions, but are brightly fluorescent upon concentration or solidification.[3] This more recent phenomenon of aggregation-induced emission (AIE) is characteristic of relatively strained molecules whose emission manifold involves orbitals on fast rotating groups such as terminal phenyl rings.[4] For instance, in tetraphenylethylene (TPE), an iconic AIE chromophore, fast rotation of the phenyl rings and partial twisting of the C=C bond quench its fluorescence in dilute solutions (Scheme 1).[5] In TPE aggregates, short intermolecular interactions obstruct the rotation of the phenyl groups and permit deactivation by fluorescence. The unique luminescence behavior of TPE and other rotors has been harnessed for the development of biological sensors,[6] solid-state lighting materials,[7] and luminescent polymers.[5,8] In all of these, short intermolecular TPE contacts are responsible for the turn-on luminescence effect.

Herein we show that tight packing of the TPE chromophores is not necessary for turn-on fluorescence, and demonstrate that anchoring AIE-type chromophores to metal ions within a rigid matrix serves as an alternative mechanism for restricting the rotation of the phenyl rings. Indeed, coordination of tetrakis(4-carboxyphenyl)ethylene (**TCPE⁴⁻**) to d^{10} ions produces luminescent MOFs wherein TPE cores are not in Van der Waals contact, yet exhibit fluorescence lifetimes similar to those of molecular aggregates (Scheme 1). Moreover, due to the spatial isolation of the chromophores, the new MOFs are porous and

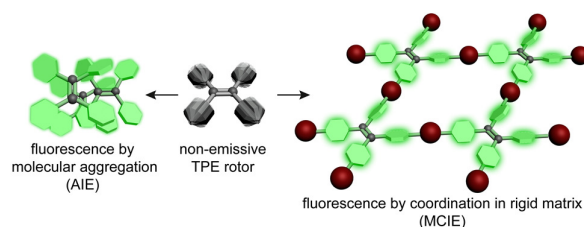**Scheme 1.** Turn-on fluorescence in a TPE rotor by aggregation (AIE) and by coordination in a rigid MOF matrix (MCIE).

fluorescence by molecular aggregation (AIE)

non-emissive TPE rotor

fluorescence by coordination in rigid matrix (MCIE)

exhibit guest-dependent emission maxima, suggesting potential applications in sensing.[9]

The new ligand **H₄TCPE** was isolated in 49 % overall yield by bromination of TPE followed by halide-for-cyanide exchange and hydrolysis of the resulting tetrakisbenzonitrile. As expected, dilute solutions of **H₄TCPE** in methanol or dimethylsulfoxide are non-emissive. However, by increasing the H₄TCPE concentration or adding a poor solvent to these dilute solutions, such as CH_2Cl_2, results in turn-on fluorescence suggesting the formation of colloidal aggregates and attesting that **H₄TCPE** is indeed AIE-active (see Figures S12-S14).

To test whether spatial separation and fluorescence could coexist, **TCPE⁴⁻** was immobilized in a rigid MOF matrix by reacting **H₄TCPE** with $Zn(NO_3)_2 \cdot 6H_2O$ in a mixture of *N,N*-diethylformamide (DEF) and ethanol at 75 °C. This reaction produced yellow block crystals of $Zn_2(C_{30}H_{16}O_8)(H_2O)_2 \cdot 4DEF$ (**1**). X-ray analysis of a crystal of **1** revealed staggered two dimensional sheets made from paddlewheel shaped $Zn_2(O_2C-)_4$
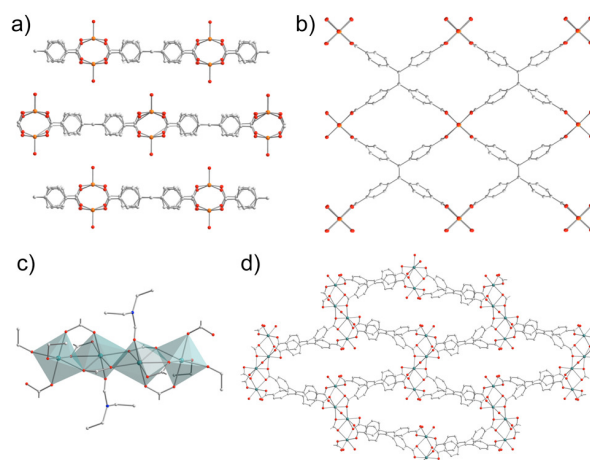

Figure 1. Portions of the X-ray crystal structures of **1** depicting (a) side- and (b) top- views of the two-dimensional sheets, and of **2** depicting (c) the Cd₄ secondary building unit, and (d) the truncated three-dimensional structure. Turquoise, orange, red, blue, and grey spheres represent Cd, Zn, O, N, and C atoms, respectively. H and guest solvent molecules atoms were omitted for clarity.
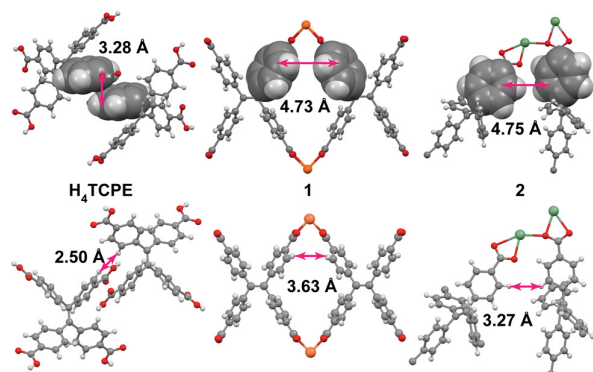
1

Figure 2. Shortest phenyl···phenyl (top) and H···H (bottom) distances in the crystal structures of **H₄TCPE**, **1**, and **2**. Turquoise, orange, red, grey, and white spheres represent Cd, Zn, O, C, and H atoms, respectively.

secondary building units (SBU) bridged by **TCPE⁴⁻** ligands (see Figures 1a and 1b). Similar reaction conditions involving Cd(NO₃)₂·4H₂O as the metal source produced yellow crystals of Cd₂(C₃₀H₁₆O₈)(DEF)(C₂H₅OH)₂·DEF (**2**).[10] X-ray analysis of a crystal of **2** revealed a structure in which tetranuclear Cd₄ units are bridged by **TCPE⁴⁻** ligands to form a neutral three-dimensional framework, shown in Figure 1d. Interestingly, despite the great variety of Cd-carboxylate SBUs already described in the MOF literature, the Cd₄ cluster in **2**, shown in Figure 1c, contains two heptacoordinate Cd²⁺ ions and has not been reported previously.[11]

Most importantly, X-ray analysis revealed that the spatial separation between the closest TPE cores in both **1** and **2** is much larger than in any reported TPE molecular derivatives. As shown in Figure 2 (top), the closest intermolecular phenyl···phenyl contacts are 4.726(1) and 4.753(1) Å, for **1** and **2** respectively. These are well over 1 Å longer than the shortest phenyl···phenyl contacts of ~3.4 Å observed for common TPE derivatives[12] and **H₄TCPE** itself, where the nearest intermolecular Ph···Ph rings are 3.28 Å apart. Moreover, the shortest H···H contacts between nearest **TCPE⁴⁻** neighbors, a parameter often cited in connection with AIE chromophores,[4,5,13] are 3.628(1) Å and 3.266(1) Å in **1** and **2**, respectively. Once again, these contacts are more than 1 Å longer than in molecular crystals of TPE derivatives, including **H₄TCPE** where the corresponding value is only 2.500(1) Å.

Despite the absence of close-packed TPE cores, which are required for fluorescence "turn-on" in AIE, both **1** and **2** are luminescent. As shown in Figure 3, they exhibit emission maxima of 480 nm and 455 nm,[14] respectively, similar to the value observed for solid **H₄TCPE**, whose emission λ_{max} is 480 nm. Furthermore, both **1** and **2** exhibit biexponential fluorescence decays composed of one short sub-nanosecond term, τ_1, and a longer term, τ_2, with values akin to those observed for **H₄TCPE**. In MOFs, short and long exponential decay terms have previously been attributed to monomer and excimer fluorescence lifetimes, respectively.[9a,20b] Because the inter-chromophore distances in **1** and **2** are well within the range of efficient energy transfer, excimer formation is likely here too. However, biexponential decays have also been observed for AIE chromophores displaying inhomogeneous phenyl ring rotation or flipping kinetics.[15] Because the dynamics of the phenyl rings in **1** and **2** are not completely suppressed (vide infra), this alternative mechanism cannot be ruled out. Solid-state NMR experiments that will distinguish between these mechanisms are underway.
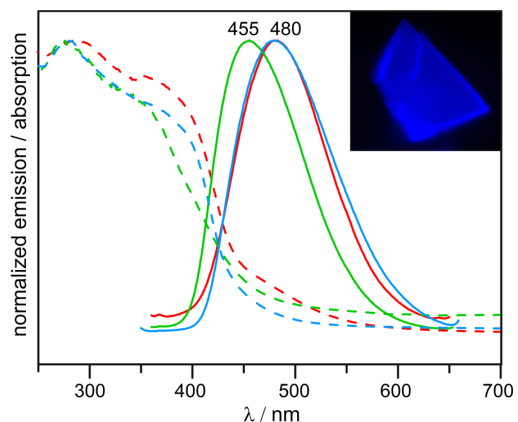

Figure 3. Diffuse reflectance (•••) and emission (—) spectra of **H₄TCPE** (—), **1** (—), **2** (—) as measured by diffuse reflectance and fluorescence spectroscopy, respectively. The inset shows an epifluorescence microscopy image for a crystal of **2**.

Altogether, the photophysical properties, which are summarized in Table 1, identify the **TCPE⁴⁻** cores as the sources of luminescence in the two MOFs. However, the structural analysis highlights an important difference between matrix coordination-induced emission (MCIE) and the AIE effect: whereas tight molecular packing turns-on fluorescence in the latter, coordinative immobilization of fluorescent **TCPE⁴⁻** cores inside rigid MOF matrices turns-on fluorescence in the former.

Although the luminescence of **1** and **2** is evident even by casual inspection by eye (see inset of Figure 3), the fluorescence quantum yields are only 1.0% and 1.8% for crystalline **1** and **2** respectively. Initially, we attributed the relatively low quantum yields to partial vibrational quenching by the guest DEF and alcohol molecules. However, thermogravimetric analysis showed that all solvent molecules can be removed from **1** by heating at 200 °C (Figure S5), and a solvent-free version of **1** displayed a similarly low quantum yield of only 2.0 %.[16] This suggests that vibrational quenching by solvent molecules is not the major excitation energy dissipation mechanism.[17] We surmise instead that the rotation of the phenyl rings is not completely shut off in **TCPE⁴⁻** despite MOF incorporation, and it therefore causes partial quenching of the fluorescence. This interpretation agrees with earlier studies of 1,4-benzenedicarboxylate-bridged MOFs, which showed that the barrier to rotation in *para*-substituted phenylenes is rather low, 11.3 ± 2 kcal/mol.[18] Partial fluorescence quenching by phenylene rotation or libration opens the intriguing possibility that *meta*-substitution on the TPE core, which should completely shut off these dissipative processes, will give rise to MOFs with improved quantum yields relative to **1** and **2**.

Table 1. Structural and photophysical properties of crystalline samples of **H₄TCPE**,[19] **1**, and **2**.

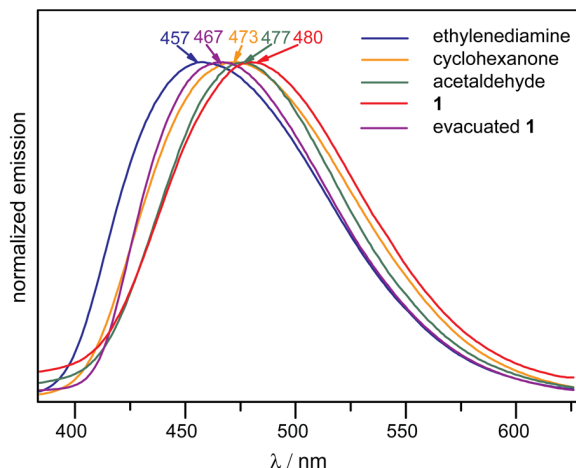|	**H₄TCPE**	**1**	**2**
shortest Ph···Ph contact, Å	3.284(1)	4.726(1)	4.753(1)
shortest H···H contact, Å	2.500(1)	3.628(1)	3.266(1)
τ_1, ns (% contribution)	0.52 (50)	0.39 (56)	0.56 (31)
τ_2, ns (% contribution)	5.54 (50)	5.90 (44)	3.30 (69)
$\phi_{fluorescence}$, %	0.8(3)	1.0(2)	1.8(6)
$\lambda_{em(max)}$, nm	480	480	455

Figure 4. Emission spectra of **1** and its desolvated version in the presence of various guest molecules.

To investigate the potential utility of TPE-based MOFs towards sensing of various analyte molecules, samples of as-synthesized **1** and **2** were heated under vacuum at 200 °C and 250 °C, respectively, and tested for permanent porosity by N_2 adsorption at 77 K. Both **1** and **2** are permanently porous with BET apparent surface areas of 317(4) m^2/g and 244(1) m^2/g, respectively, which suggested they could accommodate small test molecules such as ethylenediamine, cyclohexanone, and acetaldehyde. Significantly, crystalline samples of desolvated **1** respond differently to exposure to these analytes: a hypsochromic shift from 467 nm to 457 nm was observed after exposure to ethylenediamine, while bathochromic shifts of 6 nm and 10 nm occurred upon exposure to cyclohexanone and acetaldehyde, respectively. Although such high sensitivity of luminescent MOFs to guest molecules has been observed previously,[20] these results attest that MCIE is a powerful technique that could lead to the rational design of specific sensors.[21]

The foregoing results demonstrate the utility of using AIE-type chromophores to construct coordination assemblies with sustainable porosity. Future work will focus on improving the fluorescence quantum yields of TPE-based MOFs by changing the phenyl rings substitution pattern and on extending the MCIE approach to other rotor chromophores.

Supporting Information Available: Experimental procedures, X-ray structure refinement tables and details, NMR spectra, TGA traces, adsorption isotherms and BET statistics, additional absorp-

tion and emission spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

REFERENCES

(1) (a) Kohler, A.; Wilson, J. S.; Friend R. H. *Adv. Mater.* **2002**, *14*, 701−707. (b) Farinola, G. M.; Ragni, R. *Chem. Soc. Rev.* **2011**, *40*, 3467−3482.

(2) (a) Birks, J. B. *Photophysics of Aromatic Molecules*; Wiley: London, 1970; pp 718. (b) Tang, C. W; VanSlyke, S. A. *Appl. Phys. Lett.* **1987**, *51*, 913−915.

(3) (a) Luo, J.; Xie, Z.; Lam, J. W. Y.; Cheng, L.; Chen, H.; Qui, C.; Kwok, H. S.; Zhan, X.; Liu, Y.; Zhu, D.; Tang, B. Z. *Chem. Commun.* **2001**, 1740−1741. (b) Tang, B. Z.; Zhan, X.; Yu, G.; Sze Lee, P. P.; Liu, Y.; Zhu, D. *J. Mater. Chem.* **2001**, *11*, 2974–2978.

(4) Hong, Y.; Lam, J. W. Y.; Tang, B. Z. *Chem. Soc. Rev.* **2011**, *40*, 5361–5388.

(5) (a) Dong, Y.; Lam, J. W. Y.; Qin, A.; Liu, J.; Li, Z.; Tang, B. Z.; Sun, J.; Kwok, H. S. *Appl. Phys. Lett.* **2007**, *91*, 011111. (b) Qin, A.; Jim, C. K. W.; Tang, Y.; Lam, J. W. Y.; Liu, J.; Mahtab, F.; Gao, P.; Tang, B. Z. *J. Phys. Chem. B* **2008**, *112*, 9281−9288. (c) Hong, Y.; Lam, J. W. Y.; Tang, B. Z. *Chem. Commun.* **2009**, 4332−4353.

(6) Wang, J.-X.; Chen, Q.; Bian, N.; Yang, F.; Qi, A.-D.; Yan, C.-G.; Han, B.-H. *Org. Biom. Chem.* **2011**, *9*, 2219−2226.

(7) (a) Quartapelle Procopio, E.; Mauro, M.; Panigati, M.; Donghi, D.; Mercandelli, P.; Sironi, A.; D'Alfonso, G.; De Cola, L. *J. Am. Chem. Soc.* **2010**, *132*, 14397-14399. (b) Yuan, W. Z.; Lu, P.; Chen, S.; Lam, J. W. Y.; Wang, Z.; Liu, Y.; Kwok, H. S.; Ma, Y.; Tang, B. Z. *Adv. Mater.* **2010**, *22*, 2159−2163.

(8) (a) Yuan, W. Z.; Zhao, H.; Shen, X. Y.; Mahtab, F.; Lam, J. W. Y.; Sun, J. Z.; Tang, B. Z. *Macromolecules* **2009**, *42*, 9400-9411. (b) Chen, Q.; Wang, J.-X.; Yang, F.; Zhou, D.; Bian, N.; Zhang, X.-J.; Yan, C.-G.; Han, B.-H. *J. Mater. Chem.* **2011**, *21*, 13554−13560.

(9) (a) Bauer, C. A.; Timofeeva, T. V.; Settersten, T. B.; Patterson, B. D.; Liu, V. H.; Simmons, B. A.; Allendorf. M. D. *J. Am. Chem. Soc.* **2007**, *129*, 7136−7144. (b) Rieter, W. J.; Taylor, K. M. L.; Lin, W. *J. Am. Chem. Soc.* **2007**, *129*, 9852–9853. (c) White, K. A.; Chengelis, D. A.; Zeller, M.; Geib, S. J.; Szakos, J.; Petoud, S.; Rosi, N. L. *Chem. Commun.* **2009**, 4506–4508. (d) Feng, P. L.; Perry IV, J. J.; Nikodemski, S.; Jacobs, B. W.; Meek, S. T.; Allendorf, M. D. *J. Am. Chem. Soc.* **2010**, *132*, 15487–15489. (e) Wang, C.; Lin, W. *J. Am. Chem. Soc.* **2011**, *133*, 4232–4235. (f) Cui, Y.; Yue, Y.; Qian, G. Chen, B. *Chem. Rev.*, DOI: 10.1021/CR200101D. (g) Lee, C. Y.; Farha, O. K.; Hong, B. J.; Sarjeant, A. A.; Nguyen, S. T.; Hupp, J. T. *J. Am. Chem. Soc.* **2011**, *133*, 15858–15861.

(10) Under slightly different reaction conditions, a second MOF, $Cd_2(C_{30}H_{16}O_8)(DEF)_{0.8}(H_2O)_{1.2}(C_2H_5OH)\cdot 2DEF$ (**3**) was isolated and crystallographically characterized (see Table S1). However, despite repeated attempts, **3** could not be isolated cleanly because it always accompanied **2** as a minor product. The structural differences between **2** and **3** are highlighted in Figures S10 and S11.

(11) Tranchemontagne, D. J.; Mendoza-Cortes, J. L.; O'Keeffe, M.; Yaghi, O. M. *Chem. Soc. Rev.* **2009**, *38*, 1257−1283.

(12) as verified by a Cambridge Crystallographic Database search in October 2011.

(13) Gagnon, E.; Maris, T.; Arseneault, P.-M.; Maly, K. E.; Wuest, J. D. *Cryst. Growth Des.* **2009**, *10*, 648−657.

(14) The maxima and the shapes of the emission spectra were independent of the excitation wavelength, which was varied between 296 nm and 380 nm (see Figures S17–S19).

(15) Ren, Y.; Lam, J. W.; Dong, Y.; Tang, B. Z.; Wong, K. S. *J. Phys. Chem. B* **2005**, *109*, 1135–1140.

(16) Although a powder X-ray diffraction pattern of desolvated **1** evidences a structural change compared to as-synthesized **1** (see Fig-

ure S4), the structural change is reversible. Therefore we do not antic-ipate a change in the coordination sequence of **1** upon desolvation.

(17) Mei, J.; Wang, J.; Qin, A.; Zhao, H.; Yuan, W.; Zhao, Z.; Sung, H. H. Y.; Deng, C.; Zhang, S.; Williams, I. D.; Sun, J. Z.; Tang, B. Z. *J. Mater. Chem.*, DOI: 10.1039/C1JM12673C.

(18) Gould, S. L.; Tranchemontagne, D.; Yaghi, O. M.; Garcia-Garibay, M. A. *J. Am. Chem. Soc.* **2008**, *130*, 3246–3247.

(19) **H₄TCPE** crystallizes with four THF molecules, which are partially lost upon exposure to the atmosphere. The sample whose photophysical measurements were determined had a molecular formu-la of **H₄TCPE**·1.8THF.

(20) (a) Allendorf, M. D.; Bauer, C. A.; Bhakta, R. K.; Houk, R. J. *Chem. Soc Rev.* **2009**, *38*, 1330−1352. (b) Stylianou, K. C.; Heck, R.; Chong, S. Y.; Basca, J.; Jones, J. T. A.; Khimyak, Y. Z.; Bradshaw, D.; Rosseinsky, M. J. *J. Am. Chem. Soc.* **2010**, *132*, 4119−4130. (c) Takashima, Y.; Martinez, V.; Furukawa, S.; Kondo, M.; Shimomura, S.; Uehara, H.; Nakahama, M.; Sugimoto, K.; Kitagawa, S. *Nature Commun.* **2011**, 2−8. (d) Yanai, N.; Kitayama, K.; Hijikata, Y.; Sato H.; Matsuda, R.; Kubota, Y.; Takata, M.; Mizuno, M.; Uemura, T.; Kitagawa S. *Nature Mater.* **2011**, 787−793.

(21) Chen, J.; Law, C. C. W.; Lam, J. W. Y.; Dong, Y.; Lo, S. M. F.; Williams, I. D.; Zhu, D.; Tang, B. Z. *Chem. Mater.* **2003**, *15*, 1535–1546.