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

The MIT Faculty has made this article openly available. Please share how this access benefits you. Your story matters.
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 tetraphenylethylene 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,\(^6,7\) solid-state lighting materials,\(^7\) and luminescent polymers.\(^8\) 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 (TCPE\(^4\)) 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 exhibit guest-dependent emission maxima, suggesting potential applications in sensing.\(^9\)

The new ligand H\(_4\)TCPE 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 H\(_4\)TCPE in methanol or dimethylsulfoxide are non-emissive. However, by increasing the H\(_4\)TCPE concentration or adding a poor solvent to these dilute solutions, such as CH\(_2\)Cl\(_2\), results in turn-on fluorescence suggesting the formation of colloidal aggregates and attesting that H\(_4\)TCPE is indeed AIE-active (see Figures S12-S14).

To test whether spatial separation and fluorescence could coexist, TCPE\(^4\) was immobilized in a rigid MOF matrix by reacting H\(_4\)TCPE with Zn(NO\(_3\))\(_2\)·6H\(_2\)O in a mixture of N,N-diethylformamide (DEF) and ethanol at 75 °C. This reaction produced yellow block crystals of Zn\(_2\)(C\(_9\)H\(_8\)O\(_8\))(H\(_2\)O)\(_2\)·4DEF (1). X-ray analysis of a crystal of 1 revealed staggered two dimensional sheets made from paddlewheel shaped Zn\(_2\)(O\(_2\)C\(_4\))\(_4\)

---

**Scheme 1.** Turn-on fluorescence in a TPE rotor by aggregation (AIE) and by coordination in a rigid MOF matrix (MCIE).
secondary building units (SBU) bridged by TCPE$^+$ ligands (see Figures 1a and 1b). Similar reaction conditions involving Cd(NO$_3$)$_2$·4H$_2$O as the metal source produced yellow crystals of Cd$_4$(C$_8$H$_8$O$_4$)(DEF)$_2$C$_8$H$_8$OH$_2$·DEF (2). X-ray analysis of a crystal of 2 revealed a structure in which tetranuclear Cd$_4$ units are bridged by TCPE$^+$ 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 Cd$^{2+}$ ions and has not been reported previously.

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 HC$_4$TCPE itself, where the nearest intermolecular Ph-Ph rings are 3.28 Å apart. Moreover, the shortest H-H contacts between nearest TCPE$^+$ neighbors, a parameter often cited in connection with AIE chromophores, 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 HC$_4$TCPE 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, respectively, similar to the value observed for solid HC$_4$TCPE, whose emission $\lambda_{\text{max}}$ is 480 nm. Furthermore, both 1 and 2 exhibit biexponential fluorescence decays composed of one short sub-nanosecond term, $\tau_1$, and a longer term, $\tau_2$, with values akin to those observed for HC$_4$TCPE. In MOFs, short and long exponential decay terms have previously been attributed to monomer and excimer fluorescence lifetimes, respectively.$^{12a,20b}$ 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.$^{13}$ 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 2](image2.png)

**Figure 2.** Shortest phenyl-phenyl (top) and H-H (bottom) distances in the crystal structures of HC$_4$TCPE, 1, and 2. Turquoise, orange, red, grey, and white spheres represent Cd, Zn, O, C, and H atoms, respectively.

![Figure 3](image3.png)

**Figure 3.** Diffuse reflectance (••••) and emission (―) spectra of HC$_4$TCPE (.), 1 (―), 2 (―) as measured by diffuse reflectance and fluorescence spectroscopy, respectively. The inset shows an epifluorescence microscopy image for a crystal of 2.

<table>
<thead>
<tr>
<th></th>
<th>HC$_4$TCPE</th>
<th>1</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>shortest Ph-Ph contact, Å</td>
<td>3.28(1)</td>
<td>4.726(1)</td>
<td>4.753(1)</td>
</tr>
<tr>
<td>shortest H-H contact, Å</td>
<td>2.500(1)</td>
<td>3.628(1)</td>
<td>3.266(1)</td>
</tr>
<tr>
<td>$\tau_1$, ns (% contribution)</td>
<td>0.52 (50)</td>
<td>0.39 (56)</td>
<td>0.56 (31)</td>
</tr>
<tr>
<td>$\tau_2$, ns (% contribution)</td>
<td>5.54 (50)</td>
<td>5.90 (44)</td>
<td>3.30 (69)</td>
</tr>
<tr>
<td>$\phi_{\text{fluorescence}}$, %</td>
<td>0.8(3)</td>
<td>1.0(2)</td>
<td>1.8(6)</td>
</tr>
<tr>
<td>$\lambda_{\text{em}}$, nm</td>
<td>480</td>
<td>480</td>
<td>455</td>
</tr>
</tbody>
</table>

Table 1. Structural and photophysical properties of crystalline samples of HC$_4$TCPE.$^{19}$ 1, and 2.
respectively, and tested for permanent porosity by N
traces, adsorption isotherms and BET statistics, ad ditional absorp-
X-ray structure refinement tables and details, NMR spectra, TGA
from the MIT-Amgen Program
and his group for assistance in the use of their fl uorimeter, and
microscope. BDM acknowledges summer undergraduate s upport
Prof. Alice Ting and Mr. Daniel Liu for use of the fluorescence
phenyl rings substitution pattern and on extending the MCIE
sustainable porosity. Future work will focus on imp roving the
chromophores to construct coordination assemblies w ith
the DCIF at MIT (CHE-9808061, DBI-9729592). This work made
X-ray crystal structure of
ported in part by the NSF under award number DMR-08 19762.
use of the MRSEC Shared Experimental Facilities at MIT, sup-
Center for Excitonics, an Energy Frontier Research Center funded
by the U.S. Department of Energy, Office of Science, Office of
Basic Energy Sciences under Award Number DE-SC0001088
(MIT). Grants from the NSF also provided instrument support to
the DCIF at MIT (CHE-9808061, DBI-9729592). This work made
use of the MRSEC Shared Experimental Facilities at MIT, sup-
ported in part by the NSF under award number DMR-0819762.
We thank Dr. Peter Müller for assistance with refinement of the
X-ray crystal structure of 1. We also thank Prof. Timothy Swager
and his group for assistance in the use of their fluorimeter, and
Prof. Alice Ting and Mr. Daniel Liu for use of the fluorescence
microscope. BDM acknowledges summer undergraduate support
from the MIT-Amgen Program.

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

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:
(3) (a) Luo, J.; Xie, Z.; Lam, J. W. Y.; Cheng, L.; Chen, H.; Qui,
Commum. 2001, 1740–1741. (b) Tang, B. Z.; Zhan, X.; Yu, G.; site
(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,
(6) Wang, J.-X.; Chen, Q.; Bian, N.; Yang, F.; Qi, A.-D.; Yan,
(7) (a) Quartapelle Procopio, E.; Mauro, M.; Panigati, M.; Dong,
D.; Mancelloni, P.; Silonzi, 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.
(8) (a) Yuan, W. Z.; Zhao, H.; Shen, X. Y.; Mahtab, F.; Lam, J.
(9) (a) Bauer, C. A.; Timofeeva, T. V.; Settlesbury, T. B.; Patterson,
B. D.; Liu, V. H.; Simmons, B. A.; Allendorf, M. D. J. Am. Chem.
Chengelis, D. A.; Zeller, M.; Geib, S. J.; Szakos, J.; Petoud, S.; Rosi,
J.; Nikodemoski, S.; Jacobs, B. W.; Meek, S. T.; Allendorf, M. D. J.
Am. Chem. Soc. 2011, 133, 4232–4235. (f) Cui, Y.; Yue, Y.; Qian,
(10) Under slightly different reaction conditions, a second MOF,
Cd₃(C₂H₆O)₅(DEF)₄(H₂O)₃[C₂H₆O]₂(DEF) (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,
(12) as verified by a Cambridge Crystallographic Database search
in October 2011.
(13) Gagnon, E.; Maris, T.; Arseneault, P.-M.; Maly, K. E.; Wuest,
(14) The maxima and the shapes of the emission spectra were inde-
dependent 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.
(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 anticipate a change in the coordination sequence of I upon desolvation.


(19) H$_4$TCPE crystallizes with four THF molecules, which are partially lost upon exposure to the atmosphere. The sample whose photophysical measurements were determined had a molecular formula of H$_4$TCPE·1.8THF.
