

Electronic Supplementary Information

Crystallization-induced dual emission from metal- and heavy atom-free aromatic acids and esters

*Yongyang Gong^a, Lifang Zhao^a, Qian Peng^b, Di Fan^b, Wang Zhang Yuan^{*a}, Yongming Zhang^{*a} and Ben Zhong Tang^{cd}*

^a *Shanghai Key Lab of Electrical Insulation and Thermal Aging, School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, Shanghai 200240, China. E-mail: wzhyuan@sjtu.edu.cn (W.Z.Y.), ymzsztu@gmail.com (Y.Z.).*

^b *Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China.*

^c *Department of Chemistry, The Hong Kong University of Science & Technology, Clear Water Bay, Kowloon, Hong Kong, China.*

^d *HKUST-Shenzhen Research Institute, No. 9 Yuexing 1st RD, South Area, Hi-tech Park, Nanshan, Shenzhen 518057, China.*

Contents

Experimental section

Scheme S1. Synthetic route to (BzP)PB.

Fig. S1. QM/MM model taking TPA as an example: one central QM molecule for high layer and the surrounding 124 MM molecules for low layer.

Fig. S2 (A) Photographs for crystalline solids and solutions of (BzP)PB taken under 365-nm UV light illumination. (B) Emission spectra of (BzP)PB in THF and THF/water mixtures with varying water

fractions (f_{ws}). (C) Ratio of the emission intensity of (BzP)PB in THF/water to that in THF. Concentration for the emission measurement is 10 μ M.

Fig. S3 Excitation and emission spectra of crystalline (BzP)PB solids. With the delay time (t_d) of 0.1 ms, no obvious delayed emission was detected.

Fig. S4 Photographs of varying compounds on the TLC plates under 254- and 365-nm UV light irradiations.

Fig. S5 Partial molecular arrangement of TFTPAs-H₂O cocrystal with denoted intermolecular interactions.

Fig. S6 Normalized absorption spectra of aromatic acids and esters in ethanol. Concentration = 20 μ M.

Fig. S7 Emission spectra of IPA recorded with different t_d values.

Table S1 Single crystal data of TFTPAs·2H₂O

Table S2 Single crystal data of DMTPAs

Table S3. Energy gap between the involved singlet and triplet states

Table S4. Spin-orbit coupling between the involved singlet and triplet states

Table S5. Solution and crystal quantum yields of the luminogens

Experimental section

Materials

Absolute ethanol, methanol, petroleum ether (PE), dichloromethane (DCM) and magnesium sulfate (MgSO₄) were analytical grade and used without further purification. Terephthalic acid (TPA), isophthalic acid (IPA) and dimethyl terephthalate (DMTPA) were purchased from Sinopharm Chemical Reagent Co., Ltd. Tetrafluoroterephthalic acid (TFTPAs) was purchased from Qingzhou Aoxing Chemical Co., Ltd. Crystalline powders of TPA were used directly. TFTPAs crystals were obtained by recrystallization from water. Other crystals were grown from their ethanol solutions *via*

solvent evaporation. The oxygen free ethanol was prepared by bubbling with nitrogen for 30 min.

Instruments

Photoluminescence (PL) spectra were recorded on a Perkin-Elmer LS 55 fluorescence spectrometer. Delayed components of the crystal emissions were measured with a delay time (t_d) of ≥ 0.1 ms. Time-resolved PL experiments were conducted on an Edinburgh FLS920 fluorescence spectrometer. Photoluminescence quantum yields of aromatic acids and esters in ethanol (Φ_s) were estimated using benzene as standard ($\Phi_s = 5\%$ in cyclohexane).¹ Those of the crystals (Φ_c) were determined on a Quantaaurus-QY C11347-11 absolute PL quantum yield measurement system (Hamamatsu, Japan).

Note: In this work, all experiments were carried out at room temperature unless specified.

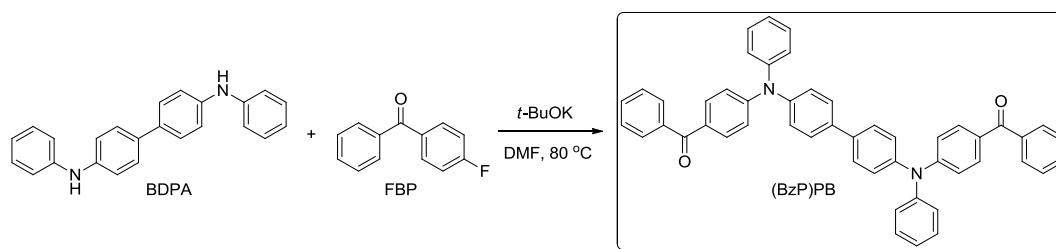
The single crystal X-ray diffraction data of TFTPAs and DMTFTPA were collected on an Agilent Xcalibur and Gemini single-crystal X-ray diffractometer using the enhanced CuK α X-ray source radiation ($\lambda = 1.54184$ Å) at 293 (TFTPAs) or 296 K (DMTFTPA) in the ω scan mode. Other crystallographic data of TPA, IPA and DMTPAs were retrieved from the Cambridge Crystallographic Data Centre (CCDC).²

Synthesis

Synthesis of dimethyl tetrafluoroterephthalate (DMTFTPA). Into a solution of tetrafluoroterephthalic acid (2.0 g) in 10 ml of methanol was added two drops of concentrated sulfuric acid under stirring. The mixture was allowed to stir at 70 °C for 12 h. Upon cooling to room temperature, it was condensed by a rotary evaporator. After being added with 0.5 M Na₂CO₃ solution, the product was extracted with DCM several times. The combined organic phase was dried over anhydrous MgSO₄. After filtration, the solution was condensed. The product was further purified by a silica column using PE/DCM (1/8 by volume) as eluent. A white solid was obtained in 72% yield (1.6 g). ¹H NMR (400 MHz, CDCl₃, δ , ppm): 3.99. ¹³C NMR (100 MHz, CDCl₃, δ , ppm): 161.02, 146.00, 143.34, 53.82. ¹⁹F NMR (376 MHz,

CDCl_3 , CF_3COOH as external standard, δ , ppm): 64.54.

Synthesis of (N,N'-bis(4-benzoyl-phenyl)-N,N'-diphenyl-benzidine) [(BzP)PB]. A mixture of *N,N'*-diphenylbenzidine (BDPA, 500.0 mg, 1.49 mmol), 4-fluorobenzophenone (FBP, 714.1 mg, 3.57 mmol) and *t*-BuOK (500.3 mg, 4.46 mmol) in *N,N'*-dimethylformamide (DMF, 50 mL) was heated to 80 °C and stirred under nitrogen for 12 h. After cooling down to room temperature, the mixture was concentrated by rotary evaporator. Then the residue was poured into cold methanol and filtered, the crude product was purified on a silica-gel column using DCM/petroleum ether as eluent. A yellow solid was obtained in 20% yield. ^1H NMR (400 MHz, CDCl_3), δ (TMS, ppm): 7.85 – 7.71 (m, 8H), 7.60 – 7.45 (m, 10H), 7.42 – 7.34 (m, 4H), 7.27 – 7.14 (m, 10H), 7.13 – 7.05 (m, 4H).



Scheme S1. Synthetic route to (BzP)PB.

Computational details

Molecular geometry optimizations were performed for the ground state (S_0) and the first excited triplet state (T_1) at the level of M06-2X/6-31G(d), and for the first excited singlet state (S_1) at the TDDFT/M06-2X/SV(P) level. The excitation energies were calculated by using TDDFT for electronic excited singlet and triplet states. Solid state effect is considered by using quantum mechanics coupled with molecular mechanics (QM/MM) theory with two-layer ONIOM method. And the computational models were built from X-ray diffractions crystal structure (see Fig. S1). The molecule in center was chosen as QM molecule and set as the high layer, whereas the remaining molecules around were treated as the MM molecules and defined as the low layer. The universal force field (UFF) was used

for the MM part, and the molecules of MM part were frozen during the QM/MM geometry optimizations. The electronic embedding are adopted in QM/MM calculations by incorporating the partial charges of the MM region into the quantum mechanical Hamiltonian. The spin-orbit coupling matrix elements were calculated at the TDDFT level³ with the first order DKH-like spin-orbit operator derived from the exact two-component Hamiltonian⁴ as implemented in BDF program package⁵. All the calculations were carried out by using Gaussian 09 program.

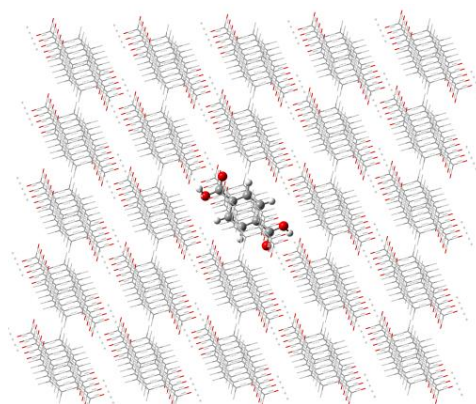


Fig. S1. QM/MM model taking TPA as an example: one central QM molecule for high layer and the surrounding 124 MM molecules for low layer.

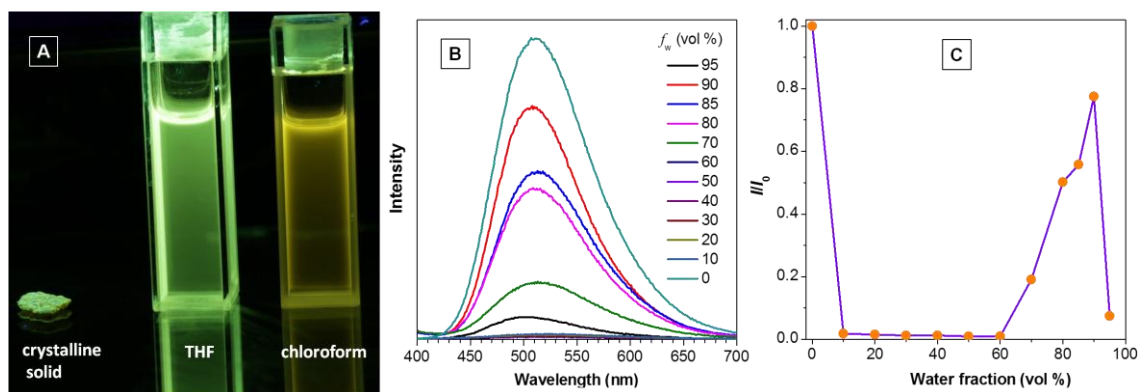


Fig. S2 (A) Photographs for crystalline solids and solutions of (BzP)PB taken under 365-nm UV light illumination. (B) Emission spectra of (BzP)PB in THF and THF/water mixtures with varying water fractions (f_w s). (C) Ratio of the emission intensity of (BzP)PB in THF/water to that in THF. Concentration for the emission measurement is 10 μ M.

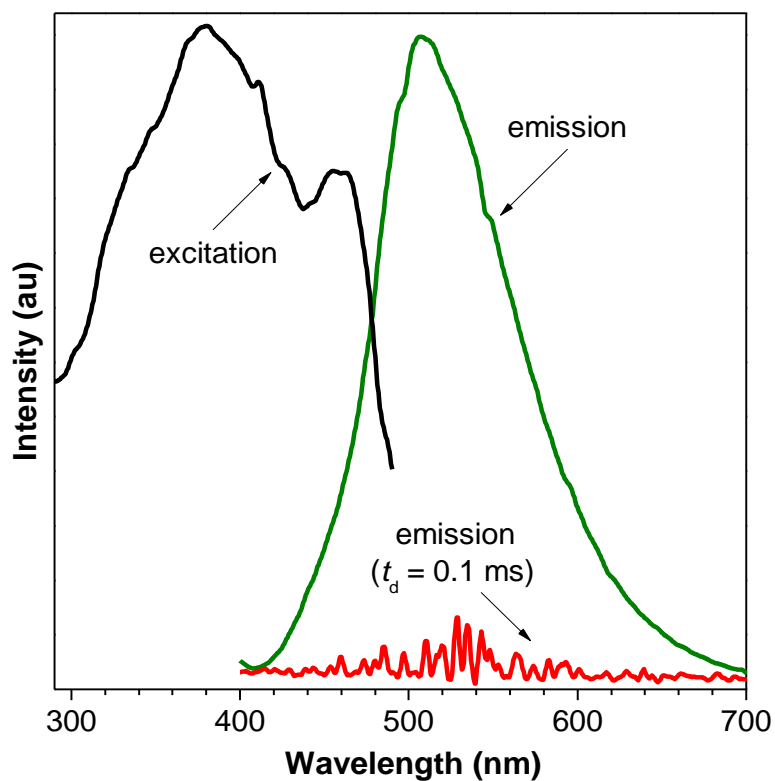


Fig. S3 Excitation and emission spectra of crystalline (BzP)PB solids. With the delay time (t_d) of 0.1 ms, no obvious delayed emission was detected.

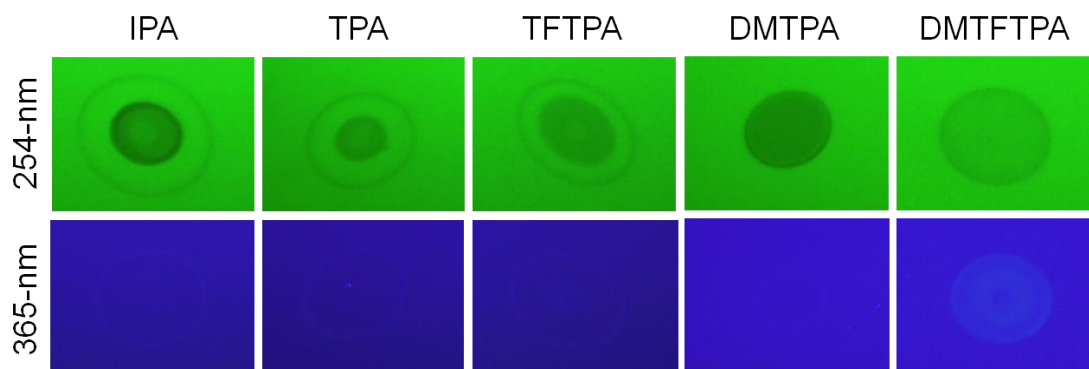


Fig. S4 Photographs of varying compounds on the TLC plates under 254- and 365-nm UV light irradiations.

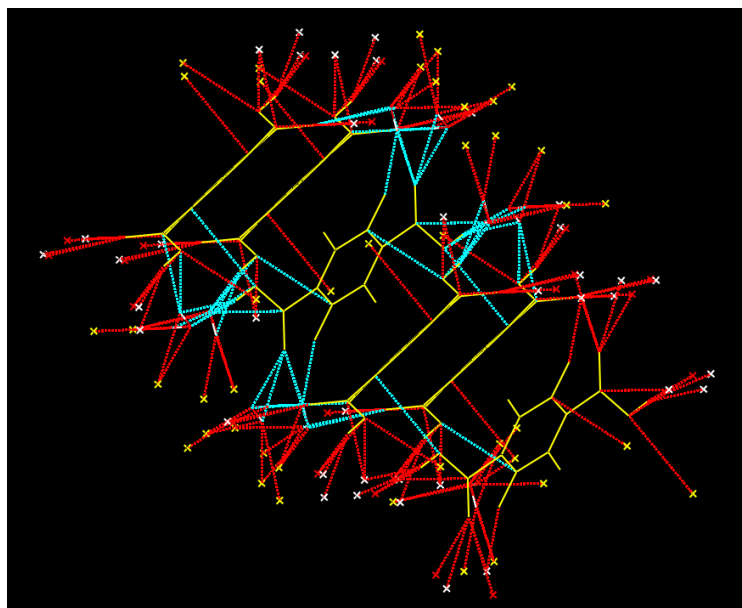


Fig. S5 Partial molecular arrangement of TFTP A-H₂O cocrystal with denoted intermolecular interactions.

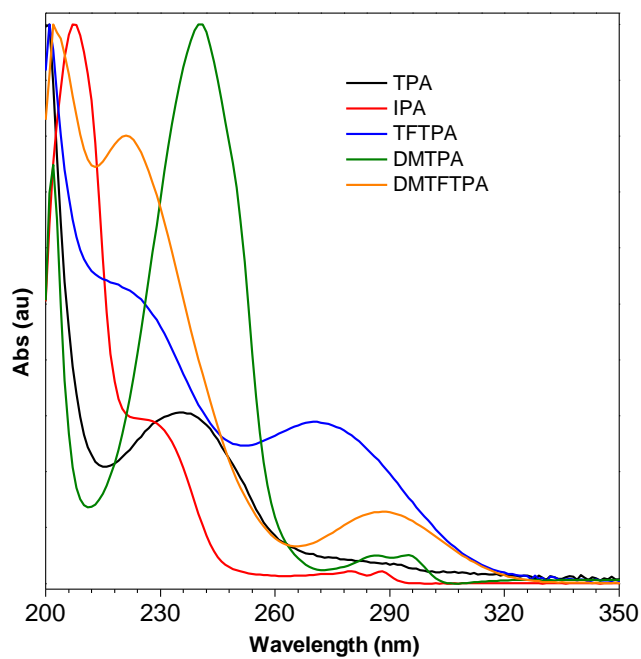


Fig. S6 Normalized absorption spectra of aromatic acids and esters in ethanol. Concentration = 20 μ M.

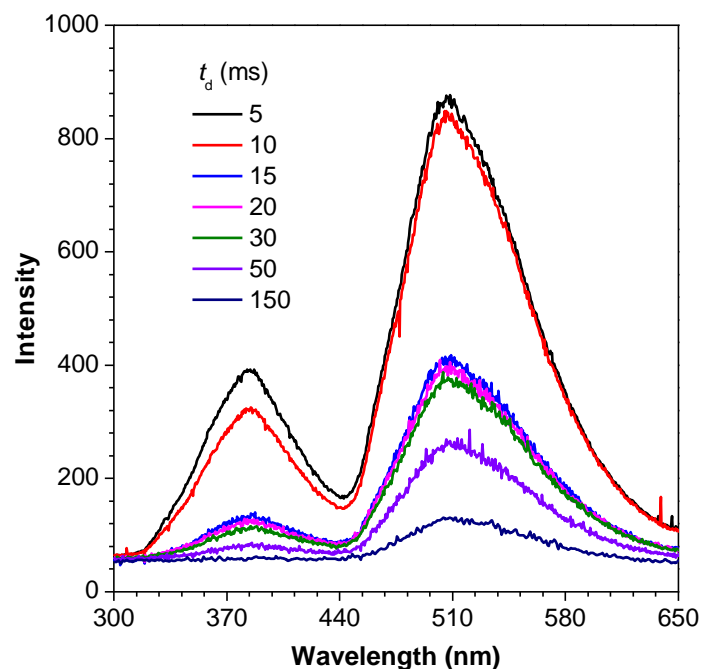


Fig. S7 Emission spectra of IPA recorded with different delay t_d values.

Table S1 Single crystal data of TFTP A · 2H₂O

Compound reference	TFTP A · 2H ₂ O
Chemical formula	C ₈ H ₆ F ₄ O ₆
Formula Mass	274.12
Crystal system	Monoclinic
$a/\text{\AA}$	8.5417(5)
$b/\text{\AA}$	8.0442(5)
$c/\text{\AA}$	7.4465(4)
$\alpha/^\circ$	90.00
$\beta/^\circ$	99.017(5)
$\gamma/^\circ$	90.00
Unit cell volume/ \AA^3	505.33(5)
Temperature/K	293(2)
Space group	P21/c
No. of formula units per unit cell, Z	4
No. of reflections measured	2808
No. of independent reflections	904
R_{int}	0.0195
Final R_I values ($I > 2\sigma(I)$)	0.0462
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.1414
Final R_I values (all data)	0.0504
Final $wR(F^2)$ values (all data)	0.1463

Table S2 Single crystal data of DMTFTPA

Compound reference	DMTFTPA
Chemical formula	C ₁₀ H ₆ F ₄ O ₄
Formula Mass	266.15
Crystal system	Monoclinic
$a/\text{\AA}$	6.332(6)
$b/\text{\AA}$	4.701(5)
$c/\text{\AA}$	17.423(16)
$\alpha/^\circ$	90.00
$\beta/^\circ$	95.605(15)
$\gamma/^\circ$	90.00
Unit cell volume/ \AA^3	516.2(9)
Temperature/K	296(2)
Space group	P2(1)/n
No. of formula units per unit cell, Z	2
No. of reflections measured	2458
No. of independent reflections	988
R_{int}	0.0453
Final R_I values ($I > 2\sigma(I)$)	0.0650
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.1877
Final R_I values (all data)	0.0709
Final $wR(F^2)$ values (all data)	0.2060

Table S3. Energy gap between the involved singlet and triplet states^a

ΔE (eV)	TPA gas	TPA crst.	IPA gas	IPA crst.	TFTPA gas	TFTPA crst.	DMTPA gas	DMTPA crst.	DMTFTPA gas	DMTFTPA crst.
S ₁ S ₀	3.669	3.606	3.652	3.467	3.948	4.022	3.236	3.889	3.523	4.055
T ₁ S ₀	3.064	2.844	3.176	3.029	2.842	2.935	2.818	3.193	2.461	2.987
T ₂ S ₀	3.294	3.377	3.277	3.148	3.524	3.542	2.958	3.513	3.208	3.565
S ₁ T ₁	0.605	0.762	0.476	0.438	1.206	1.087	0.418	0.696	1.062	1.068
S ₁ T ₂	0.375	0.229	0.375	0.319	0.424	0.480	0.378	0.376	0.315	0.490

^a ΔE : energy gap between different states.**Table S4.** Spin-orbit coupling between the involved singlet and triplet states^a

ζ (cm ⁻¹)	TPA gas	TPA crst.	IPA gas	IPA crst.	TFTPA gas	TFTPA crst.	DMTPA gas	DMTPA crst.	DMTFTPA gas	DMTFTPA crst.
S ₀ T ₁	7.16	12.36	14.39	26.31	0.04	0.01	25.69	0.69	8.82	0.0
S ₁ T ₁	17.69	13.38	17.05	5.22	0.02	0.34	3.06	16.97	0.03	0.36
S ₁ T ₂	4.71	11.02	10.27	20.00	0.42	1.03	18.32	0.39	0.37	1.23
f	0.0001	0.0055	0.0001	0.0001	0.074	0.073	0.0001	0.0001	0.062	0.069

^a ζ : spin-orbit coupling; f : oscillator strength.

Table S5. Solution and crystal quantum yields of the luminogens^a

sample	Φ_s (%)					Φ_c (%)	
	1	2	3	$\overline{\Phi_s}$	s		e
TPA	0.50	0.64	0.58	0.57	0.07	8.4	0.3
IPA	0.31	0.26	0.43	0.33	0.09	15.3	0.3
TFTPA	0.27	0.33	0.31	0.30	0.03	2.0	0.3
DMTPA	0.09	0.10	0.09	0.09	0.01	1.5	0.3
DMTFTPA	0.40	0.44	0.38	0.40	0.05	2.7	0.3

^a Φ_s = solution efficiency, determined for three times using benzene as standard ($\Phi_s = 5\%$ in cyclohexane); $\overline{\Phi_s}$ = mean efficiency; $s = \sqrt{\frac{\sum_{i=1}^n (\Phi_{s,i} - \overline{\Phi_s})^2}{n-1}}$, refers to standard error; Φ_c = crystal efficiency, determination at different times gives almost the same value; e = instrument error.

References

- 1 W. R. Dawson and M. W. Windsor, *J. Phys. Chem.*, 1968, **72**, 3251.
- 2 TPA: M. Bailey and C. J. Brown, *Acta Crystallogr.*, 1967, **22**, 387; (b) IPA: J. L. Derissen, *Acta Crystallogr. Sect. B*, 1974, **30**, 2764; (c) DMTPA: F. Brisse and S. Perez, *Acta Crystallogr. Sect. B*, 1976, **32**, 2110.
- 3 Z. D. Li, B. Suo, Y. Zhang, Y. L. Xiao and W. J. Liu, *Mol. Phys.*, 2013, **111**, 3741.
- 4 Z. D. Li, Y. L. Xiao and W. J. Liu, *J. Chem. Phys.*, 2012, **137**, 154114.
- 5 W. J. Liu, G. Hong, D. Dai, L. M. Li and M. Dolg, *Theor. Chem. Acc.*, 1997, **96**, 75.