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Supporting Information

Triarylmethanolation as a Versatile Strategy to Convert PAHs into Amorphization Induced Emission Luminogens for Extremely Sensitive Explosive Detection and Artificial Light-Harvesting Systems

Min Su, [a,b] Ya-Nan Jing, [a] Hongli Bao *[a.b] and Wen-Ming Wan *[a,b,c]

[a] Key Laboratory of Coal to Ethylene Glycol and Its Related Technology, State Key Laboratory of Structural Chemistry, Center for Excellence in Molecular Synthesis, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, 155 Yangqiao Road West, Fuzhou, Fujian 350002, P. R. China.

[b] University of Chinese Academy of Sciences, Beijing, 100049, P. R. of China

[c] State Key Laboratory of Molecular Engineering of Polymers (Fudan University), Shanghai, 200438, P. R. of China.

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Experimental details

Materials

THF Solvents were dried by Inert PureSolv MD5 before being used for the synthesis. chemicals and all other solvents used throughout the experiment were analytical-grade and were used without further purification.

Instrumentations

^{1}H and ^{13}C NMR spectra were recorded on Bruker-BioSpin AVANCE III HD and JEOL ECZ600S. Data for ^{1}H NMR spectra are reported relative to chloroform as an internal standard (7.26 ppm) and are reported as follows: chemical shift (ppm), multiplicity, coupling constant (Hz), and integration. Data for 13C NMR spectra are reported relative to chloroform as an internal standard (77.23 ppm) and are reported in terms of chemical shift (ppm). UV-vis absorption spectra of solution were recorded in THF on a Shimadzu UV-2450 UV-Vis spectrophotometer at room temperature. Photoluminescence (PL) spectra of solid samples were recorded on the Edinburgh Instruments FLS1000 three-monochromator spectrophotometer and the absolute fluorescence quantum yield was measured with an integrating sphere. Photoluminescence (PL) spectra of sample solutions were measured on the Edinburgh Instruments FLS5 fluorescence spectrofluorometer. The micro-area Photoluminescence (PL) spectra of single crystal TAM-An were collected in Nikan Ti-U Fluorescence microscopy with Spectrometer (Acton SpectraPro SP-2300) and DAPY filter (λ ex = 361-389 nm) token off BA filter (430-490 nm). The Field emission scanning electron microscopy (FESEM) images were obtained on Regulus-8100 microscope. The powder X-ray diffraction (PXRD) measurements were performed by Rikagu Miniflex600 Benchtop X-ray Diffractometer instrument with Cu Kα radiation (λ = 1.5406 Å). Single crystal X-ray diffraction were carried out on Rikagu Synergy Custom (Liquid MetalJet D2 Plus) diffractometer using Ga Kα radiation (λ = 1.3405 Å). Data collection and unit cell refinement were executed by using CrysAlisPro software. Data processing and absorption correction, giving minimum and maximum transmission factors, were accomplished with CrysAlisPro. The structure was solved with the SHELXT and refined with the SHELXL using Least Squares minimisation. Crystal data and structure refinements of TAM-Py, Pyrene and TAM-An are listed in Table S2, Table S3 and Table S4, respectively. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via https://www.ccdc.cam.ac.uk/.

Characterization methods

Aggregation-induced emission (AIE) measurements. The measurements of the TAM-Py, TAM-An, and Pyrene were tested in water/THF mixtures. The fluorescence spectra of compounds in water/THF mixtures with different water content were recorded immediately on an Edinburgh Instruments FLS5 fluorescence spectrofluorometer.

Light harvesting measurements. The light harvesting systems were prepared by adding the mixtures of TAM-Py (5.0 mg/mL in THF) with different amounts of NiR (1.0 mg/mL in THF) to a colorimeter followed by addition of the water and the concentration of TAM-Py was fixed at 0.5 mg/mL. The fluorescence spectra of TAM-Py in 90% water/THF mixtures (vol%) were recorded immediately on an Edinburgh Instruments FLS5 fluorescence spectrofluorometer and the fluorescence lifetime decays were collected on the Edinburgh Instruments FLS1000 with an uF2 pulse lamp.

Calculations of energy-transfer efficiency (ΦET) and antenna effect. (1) Energy-transfer efficiency (ΦET), the fraction of the absorbed energy that is transferred to the acceptor is experimentally measured as a ratio of the fluorescence intensities of the donor in the absence and presence of the acceptor (I_D and I_{DA}).[1]

$$\Phi_{ET} = 1 - \frac{I_{DA}}{I_D}$$

(2) The antenna effect under certain concentrations of donor and acceptor equals the ratio of the emission intensity at 620 nm of the acceptor upon excitation of the donor. $I_{A+D(ex\,=\,364\,nm)}^{620\,nm} - I_{D\,(ex\,=\,364\,nm)}^{620\,nm}$, to that of the direct excitation of the acceptor,. $I_{A+D\,(ex\,=\,458\,nm)}^{620\,nm}$.

$$\text{Antenna effect} = \frac{I_{A+D\,(ex\,=\,364\,nm)}^{620\,nm} - I_{D\,(ex\,=\,364\,nm)}^{620\,nm}}{I_{A+D(ex\,=\,458\,nm)}^{620\,nm}}$$

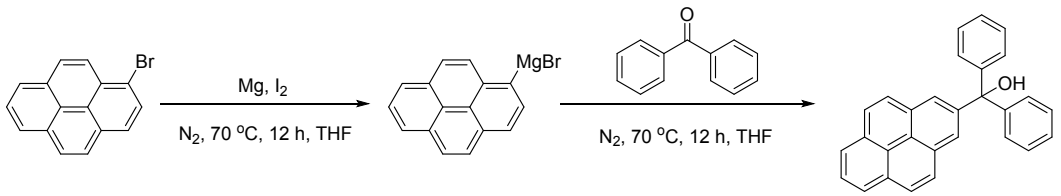
The detection of 2,4,6-trinitrotoluene (TNT). The detection was done in 95% water/THF mixtures (vol%) and the concentration of TAM-Py was fixed at 1mM. The fluorescence spectra of THF with different amounts of TNT were recorded respectively on an Edinburgh Instruments FLS5 fluorescence spectrofluorometer. Meanwhile, test strips for the detection of TNT powder were made by dripping TAM-Py solution onto the filter papers and then dried it in air which showed cyan fluorescence under irradiation with UV lamp @ 365 nm. The residual TNT was simulated by dripping TNT methanol solution with concentration of 0.1 mg/mL on the glass substrate then left to volatilize until no solvent. After wiping the glass substrate coated with TNT powder, the test strips became non-emissive under UV lamp. The minimum amount of TNT powder for naked eye detection was 250 ng (taking 2.5 μL of 0.1mg/mL TNT solution in methanol).

Theoretical calculation. All the molecules were fully optimized by density functional theory (DFT) methods with the B3LYP hybrid functional and the 6-311G* basis set implemented in the Gaussian 09 package. The vertical excitations and the excited state structure optimizations were

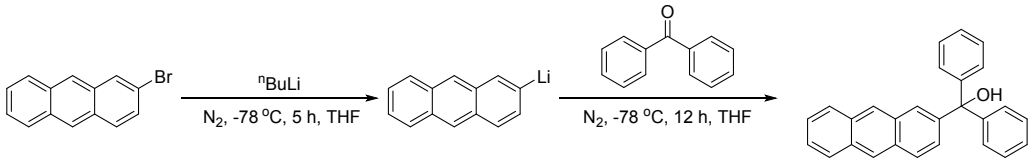
performed using the time-dependent extension of DFT (TD-DFT) with the same functional and basis set. The environment layer is treated with the universal force field (UFF). All the atoms are allowed to relax both in the ground and excited state calculations.

Synthesis

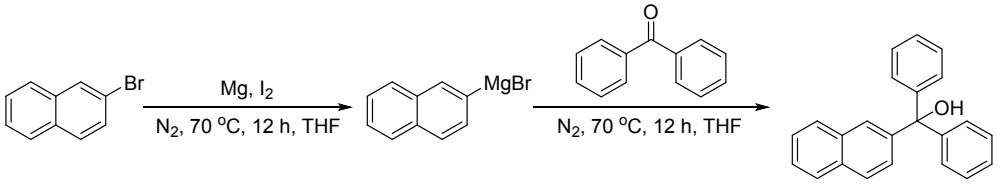
Synthesis of diphenyl(pyren-1-yl)methanol (TAM-Py). To one flame-dried Schlenk tube containing of freshly peeled Mg scraps (2.0 mmol, 2.4 equiv.), dry THF (15 mL) and a particle of iodine were added under N_2. Then 1-bromopyrene (10.0 mmol, 2 equiv.) dissolved in THF (5 mL) was slow added to the flask through a syringe at rt. The resulting mixture was stirred at 70 ^oC for 12 h before adding slowly benzophenone (5.0 mmol, 1 equiv.) dissolved in THF (5 mL). After the reaction continued at 70 ^oC for 12 h, the solution was cooled to room temperature, followed by quenching and hydrolysis with saturated aqueous ammonium chloride. After filtration and workup with dichloromethane/water, the organic solution was dried with anhydrous $MgSO_4$. Then the solvent was removed by rotary evaporation under vacuum and the residue was chromatographed on silica gel (petroleum ether/ethyl acetate = 20:1) to yield TAM-Py (1.382 g, 72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (d, *J* = 9.4 Hz, Ar*H*, 1 H), 8.17 (d, *J* = 7.5 Hz, Ar*H*, 1 H), 8.13 – 7.94 (m, Ar*H*, 5 H), 7.88 (d, *J* = 9.5 Hz, Ar*H*, 1 H), 7.45 (d, *J* = 8.1 Hz, Ar*H*, 1 H), 7.40 – 7.30 (m, Ar*H*, 10 H), 3.53 (s, O*H*, 1 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.59 (Ar*C*), 140.12 (Ar*C*), 131.55 (Ar*C*), 131.38 (Ar*C*), 130.46 (Ar*C*), 129.66 (Ar*C*), 128.28 (Ar*C*H), 128.10 (Ar*C*H), 128.04 (Ar*C*H), 127.87 (Ar*C*H), 127.47 (Ar*C*H), 127.43 (Ar*C*H), 127.15 (Ar*C*H), 126.96 (Ar*C*H), 126.21 (Ar*C*H), 126.16 (Ar*C*), 125.51 (Ar*C*H), 125.46 (Ar*C*H), 124.89 (Ar*C*), 123.77 (Ar*C*H), 83.86 (*C*OH) ppm.



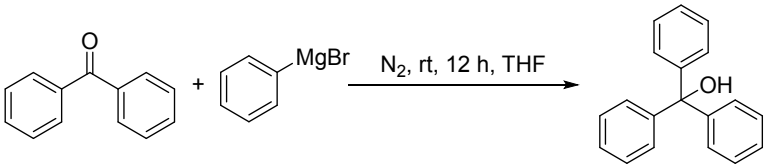
Synthesis of anthracen-2-yldiphenylmethanol (TAM-An). To one flame-dried Schlenk tube containing of 2-bromoanthracene (4.8 mmol, 1.2 equiv.) dissolved in dry THF (10 mL) at -78 ^oC, n-butyllithium (2.5 M in hexane, 6.0 mmol, 1.5 equiv.) was added by slow dropwise addition over 5 min and stirred for 5 h under N_2. Then benzophenone (4.0 mmol, 1 equiv.) dissolved in THF (5 mL) was added by slow dropwise addition over 2 min, and the resulting mixture was stirred with the temperature maintained -78 ^oC for 12 h. Next, the solution was cooled to room temperature, followed by quenching and hydrolysis with saturated aqueous ammonium chloride. After filtration and workup with dichloromethane/water, the organic solution was dried with anhydrous $MgSO_4$. Then the solvent was removed by rotary evaporation under vacuum and the residue was chromatographed on silica gel (petroleum ether/ethyl acetate = 20:1) to yield TAM-An (905 mg, 63%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (s, Ar*H*, 1 H), 8.32 (s, Ar*H*, 1 H), 8.03 – 7.92 (m, Ar*H*, 3 H), 7.78 (d, J = 1.8 Hz, Ar*H*, 1 H), 7.51 – 7.42 (m, Ar*H*, 3 H), 7.42 – 7.29 (m, Ar*H*, 10 H), 2.96 (s, O*H*, 1 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.59 (Ar*C*), 143.58 (Ar*C*), 132.17 (Ar*C*), 132.13 (Ar*C*), 131.12 (Ar*C*), 130.97 (Ar*C*), 128.34 (Ar*C*H), 128.33 (Ar*C*H), 128.27 (Ar*C*H), 128.23 (Ar*C*H), 127.64 (Ar*C*H), 127.13 (Ar*C*H), 126.74 (Ar*C*H), 126.31 (Ar*C*H), 126.01 (Ar*C*H), 125.67 (Ar*C*H), 125.63 (Ar*C*H), 82.48 (*C*OH) ppm.



Synthesis of naphthalen-2-yldiphenylmethanol (TAM-Na). Following the procedure for the synthesis of TAM-Py, TAM-Na was obtained as a white solid (1.333g, 86%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.89 – 7.71 (m, Ar*H*, 4 H), 7.55 – 7.46 (m, Ar*H*, 3 H), 7.42 – 7.30 (m, Ar*H*, 10 H), 3.05 – 2.97 (m, O*H*, 1 H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ 146.84 (Ar*C*), 144.33 (Ar*C*), 132.93 (Ar*C*), 132.67 (Ar*C*), 128.62 (Ar*C*H), 128.20 (Ar*C*H), 127.86 (Ar*C*H), 127.66 (Ar*C*H), 127.55 (Ar*C*H), 126.71 (Ar*C*H), 126.54 (Ar*C*H), 126.38 (Ar*C*H), 126.32 (Ar*C*H), 82.37 (*C*OH) ppm.



Synthesis of triphenylmethanol (TAM-Ph). To one flame-dried Schlenk tube containing of benzophenone (5.0 mmol, 1 equiv.), dry THF (10 mL) was added under N_2. Then phenylmagnesium bromide (1 M in THF, 6.0 mmol, 1.2 equiv.) was slow added to the flask through a syringe at rt. After the reaction was stirred at rt for 12 h, the resulting mixture was quenched and hydrolyzed with saturated aqueous ammonium chloride. After filtration and workup with dichloromethane/water, the organic solution was dried with anhydrous $MgSO_4$. Then the solvent was removed by rotary evaporation under vacuum and the residue was chromatographed on silica gel (petroleum ether/ethyl acetate = 20:1) to yield TAM-Ph. (1.028 g, 79%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.02 (m, Ar*H*, 15 H), 2.82 (s, O*H*, 1 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.03 (Ar*C*), 128.13 (Ar*C*H), 128.12 (Ar*C*H), 127.46 (Ar*C*H), 82.22 (*C*OH) ppm.



Supplementary Figures

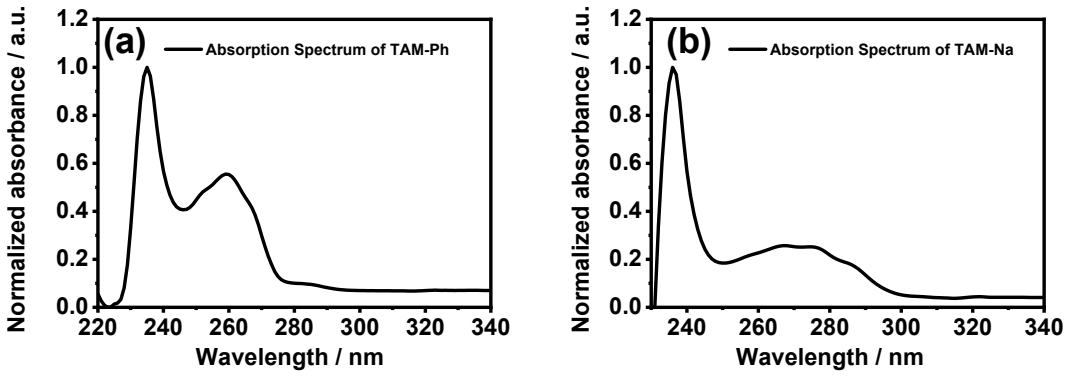


Fig. S1 (a) Absorption spectrum of TAM-Ph in THF. (b) Absorption spectrum of TAM-Na in THF.

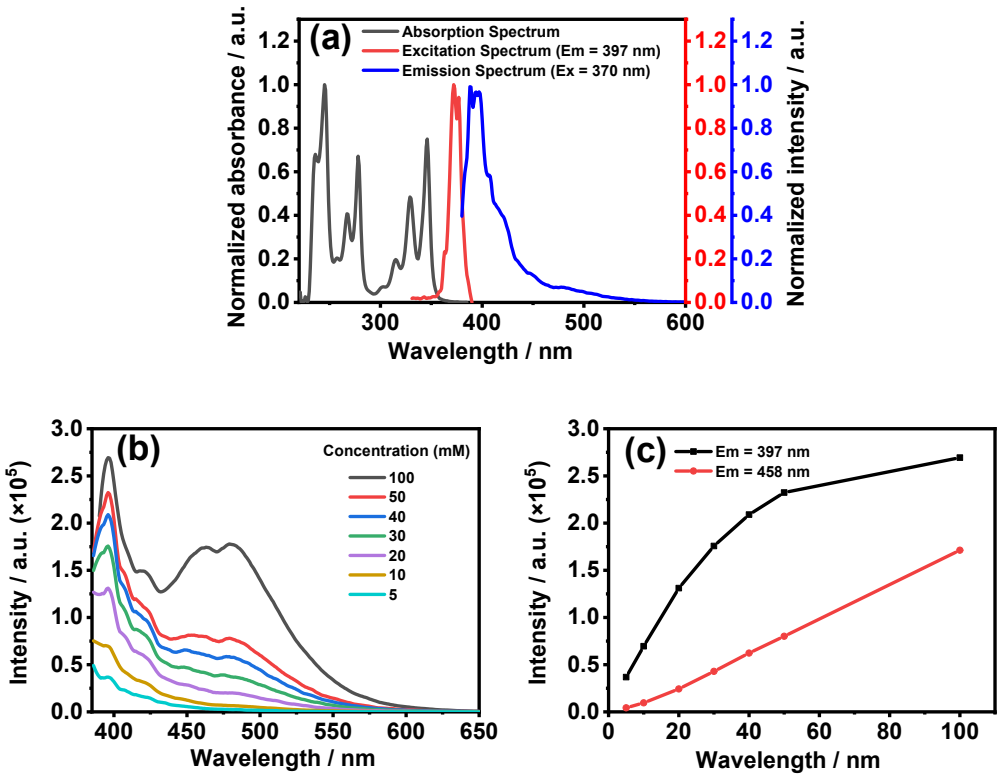


Fig. S2 Photophysical properties of TAM-Py. (a) Absorption spectrum, excitation spectrum and emission spectrum of solution (solution concentration = 10 mM, THF). (b) Emission spectra and (c) the change in relative emission intensity at 397 nm and 458 nm for TAM-Py in THF solutions with different concentrations; excitation wavelength = 384 nm.

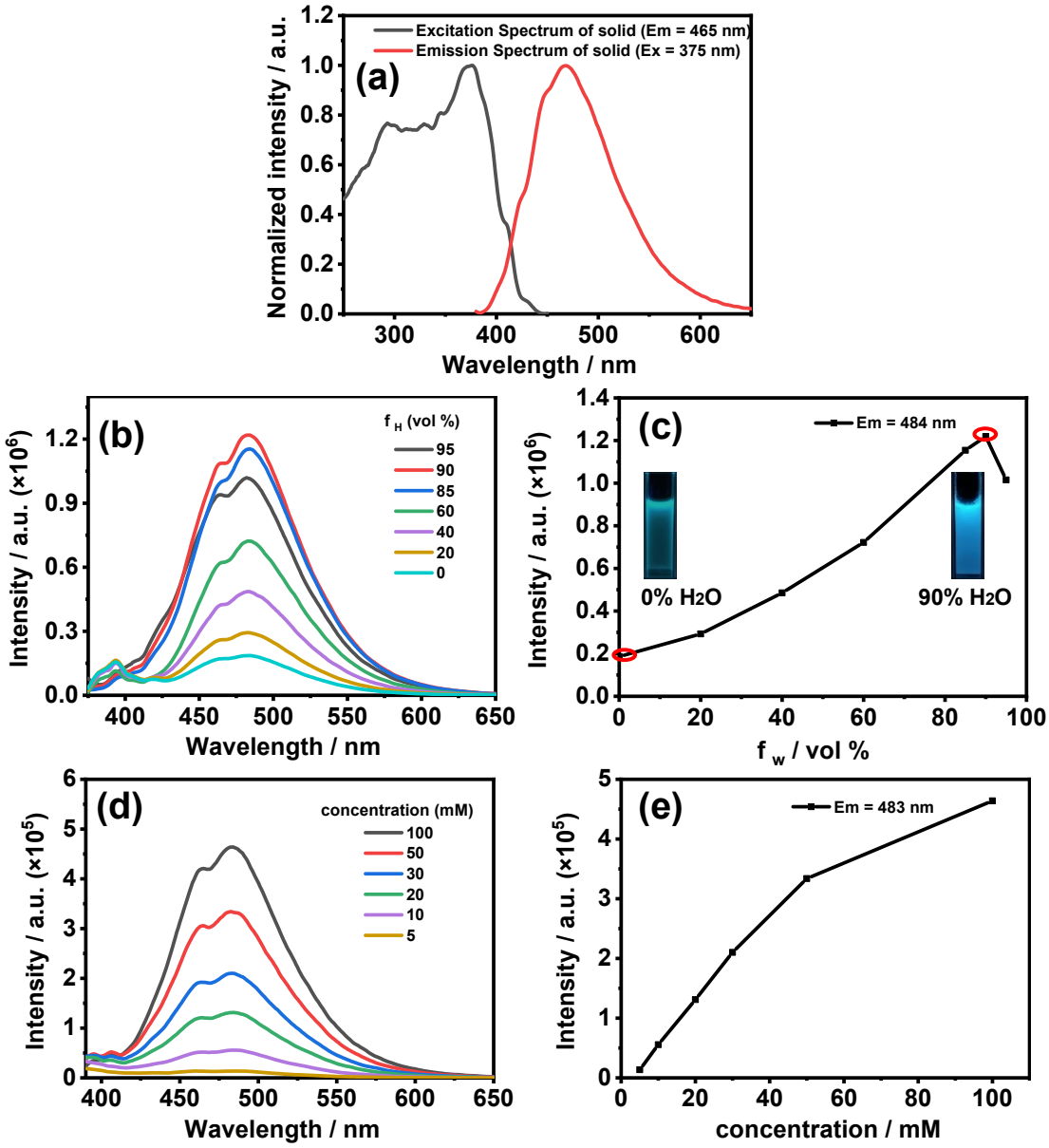


Fig. S3 Photophysical properties of Pyrene. (a) Excitation spectrum and emission spectrum of solid (amorphous state). (b) Emission spectra in 10 mM water/THF mixtures with different water volume fractions (*f* w, vol%); excitation wavelength = 370 nm. (c) Plot of relative emission intensity at 484 nm. Inset in (c): Photographic images in 0% and 90% water/THF mixtures (vol%) under irradiation with UV lamp @ 365 nm; (d) Emission spectra and (e) the change in relative emission intensity at 483nm in THF solutions with different concentrations; excitation wavelength = 383 nm.

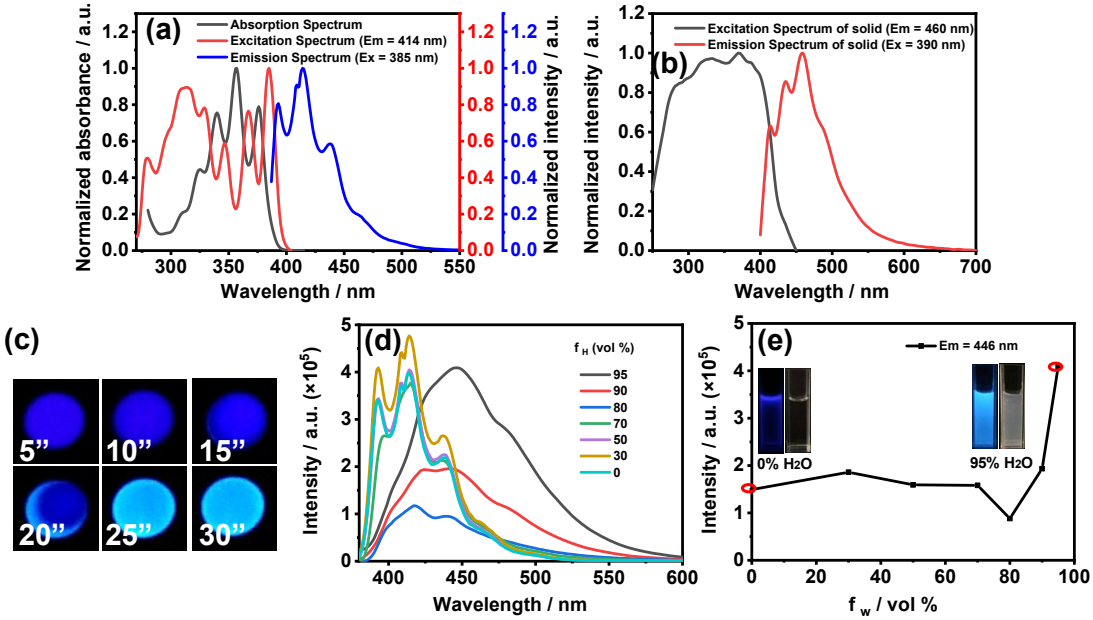


Fig. S4 Photophysical properties of TAM-An. (a) Absorption spectrum, excitation spectrum and emission spectrum of solution (solution concentration = 1 mM, THF). (b) Excitation spectrum and emission spectrum of solid (amorphous state). (c) Photographic images of one drop of TAM-An solution on thin-layer chromatography under irradiation with UV lamp @ 365 nm. (d) Emission spectra of TAM-An in 1 mM water/THF mixtures with different water volume fractions (*f* w, vol %); excitation wavelength = 375 nm. (e) Plot of relative emission intensity at 446 nm. Inset in (e): Photographic images of TAM-An in 0% and 95% water/THF mixtures (vol%) under sunlight and irradiation with UV lamp @ 365 nm, respectively.

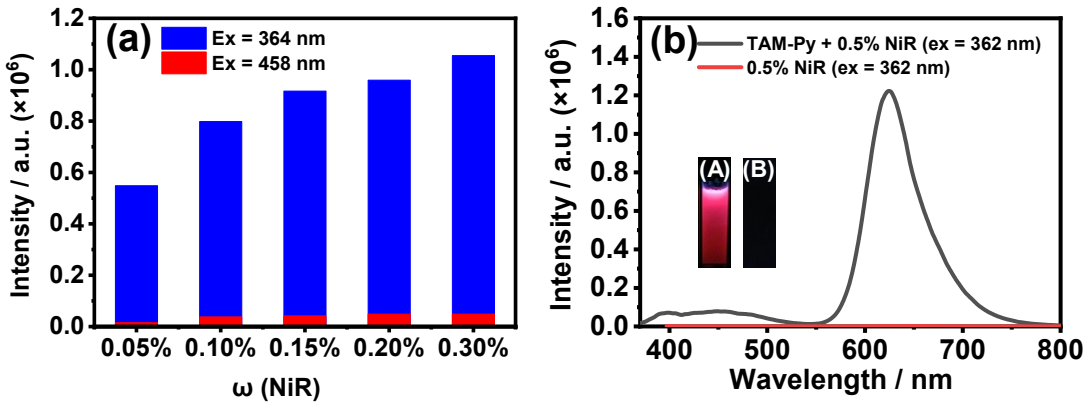


Fig. S5 (a) The histogram of the TAM-Py emission intensities at 620 nm with different amounts of NiR excited at 364 nm and 458 nm, respectively. (b) Emission spectra of TAM-Py + 0.5% NiR (ex = 362 nm), and 0.5% NiR (ex = 362 nm). Inset in (b): (A) Photographic images of TAM-Py + 0.5% NiR and (B) 0.5% NiR under irradiation with UV lamp @ 365 nm. [TAM-Py] = 0.5 mg/mL in 90% water/THF mixtures (vol%). The ratios are based on weight ratio of TAM-Py.

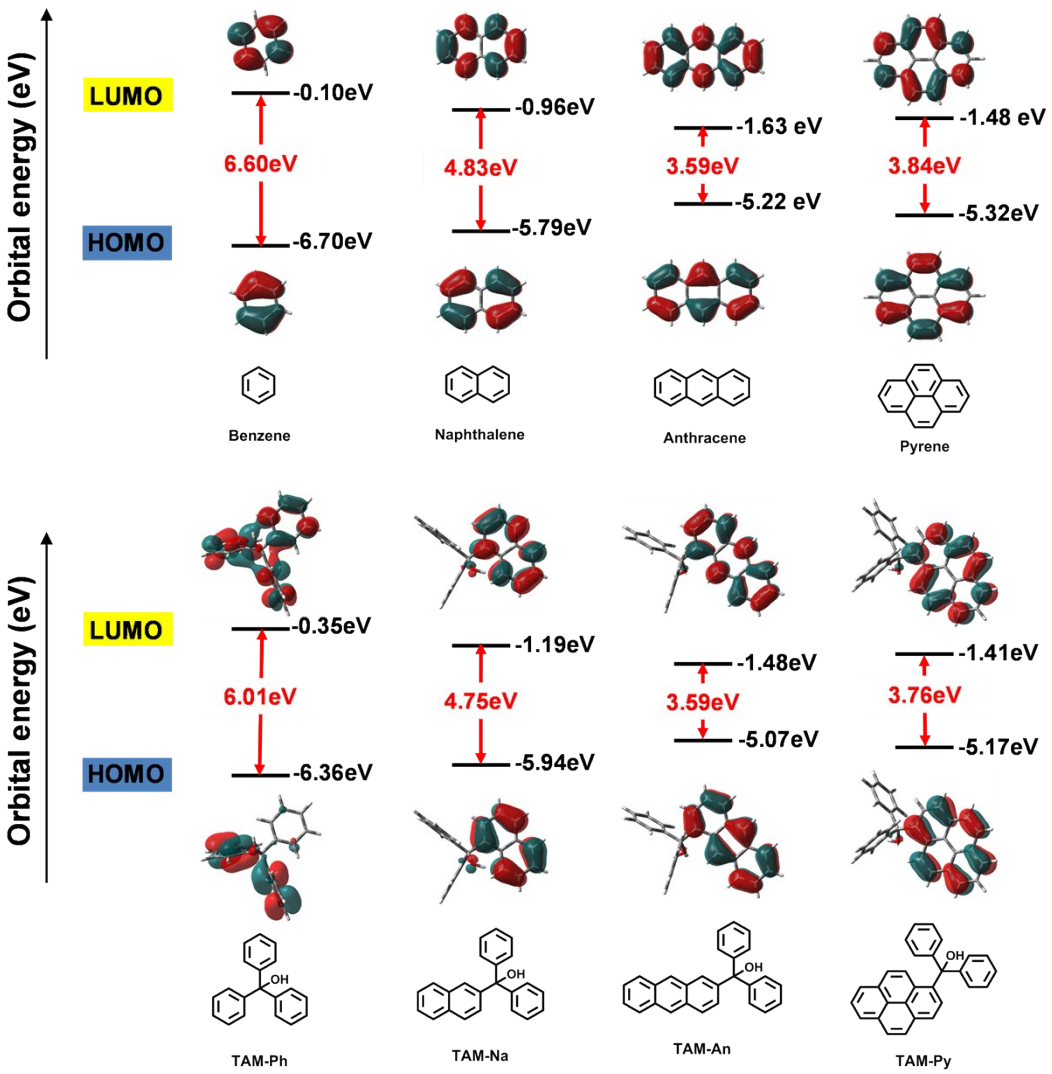


Fig. S6 Energy levels (eV) of Benzene, Naphthalene, Anthracene, Pyrene, TAM-Ph, TAM-Na, TAM-An and TAM-Py in the excited state calculated by TD-DFT B3LYP/6-311G*, Gaussian 09 program.

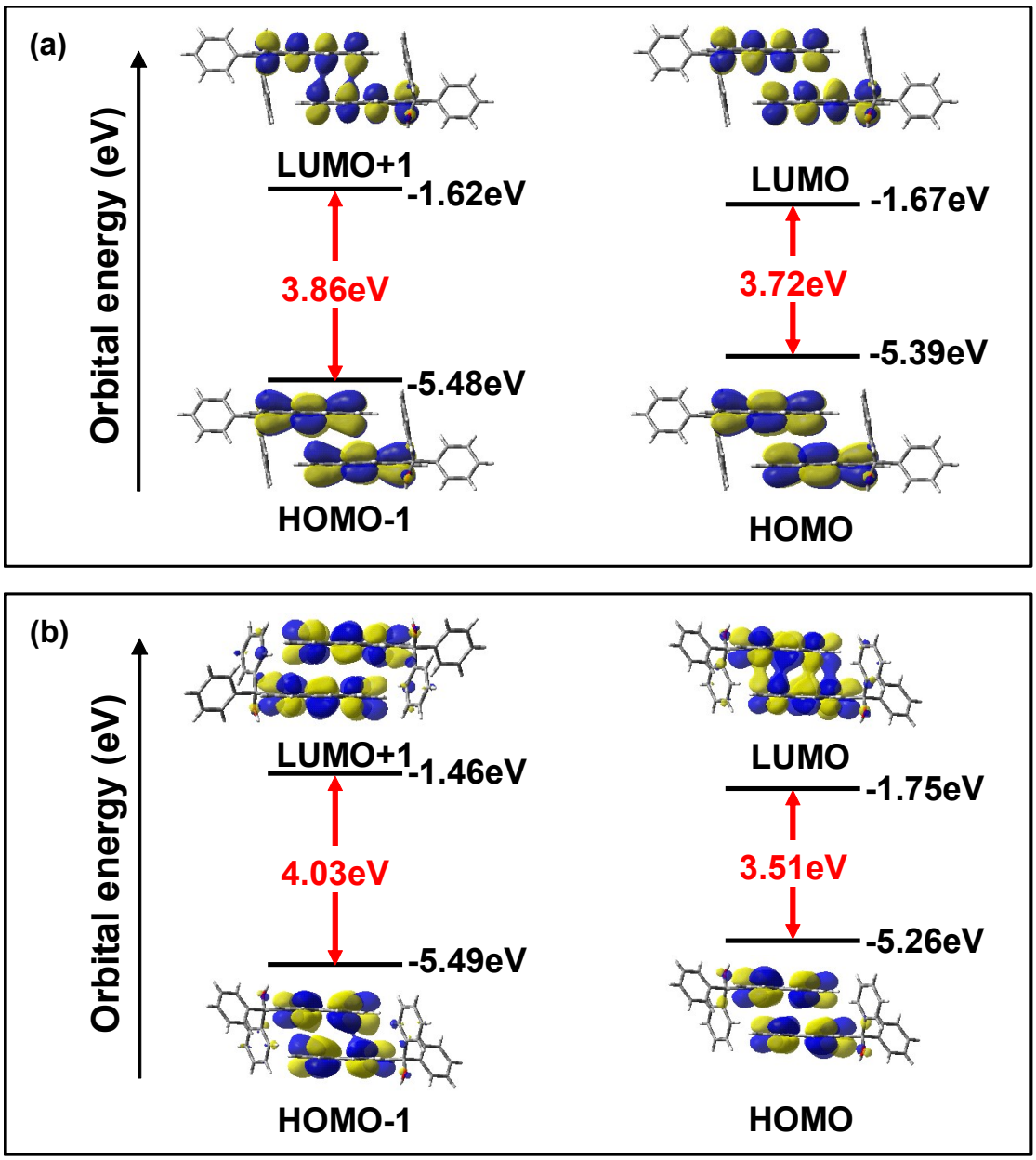


Fig. S7 Energy levels (eV) of (a) TAM-Py single crystal structure and (b) stronger π- π stacking than single crystal structure in the excited state calculated by TD-DFT B3LYP/6-311G*, Gaussian 09 program.

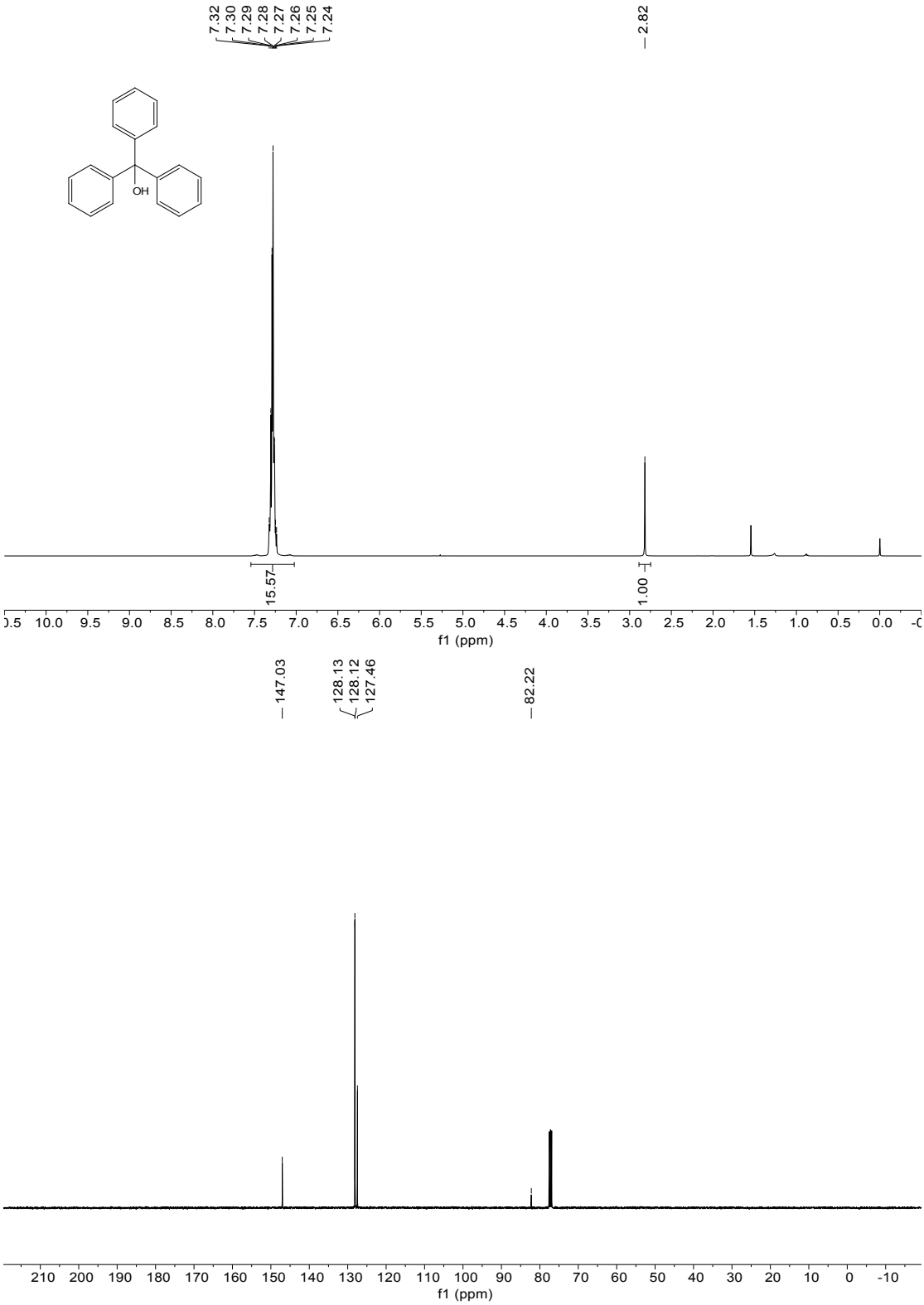


Fig. S8 ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of TAM-Ph in $CDCl_3$

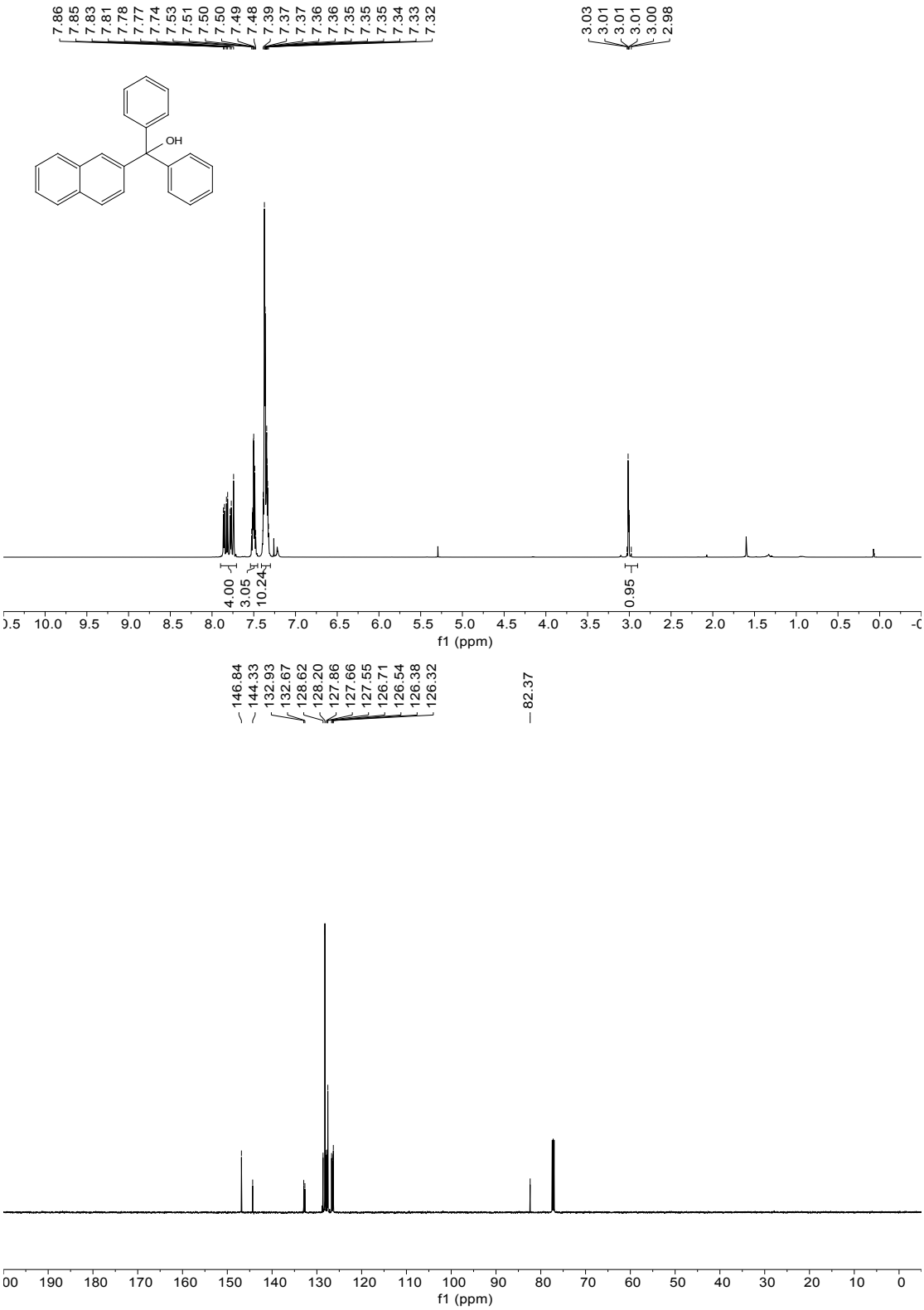


Fig. S9 ^{1}H (600 MHz) and ^{13}C (150 MHz) NMR spectra of TAM-Na in $CDCl_3$.

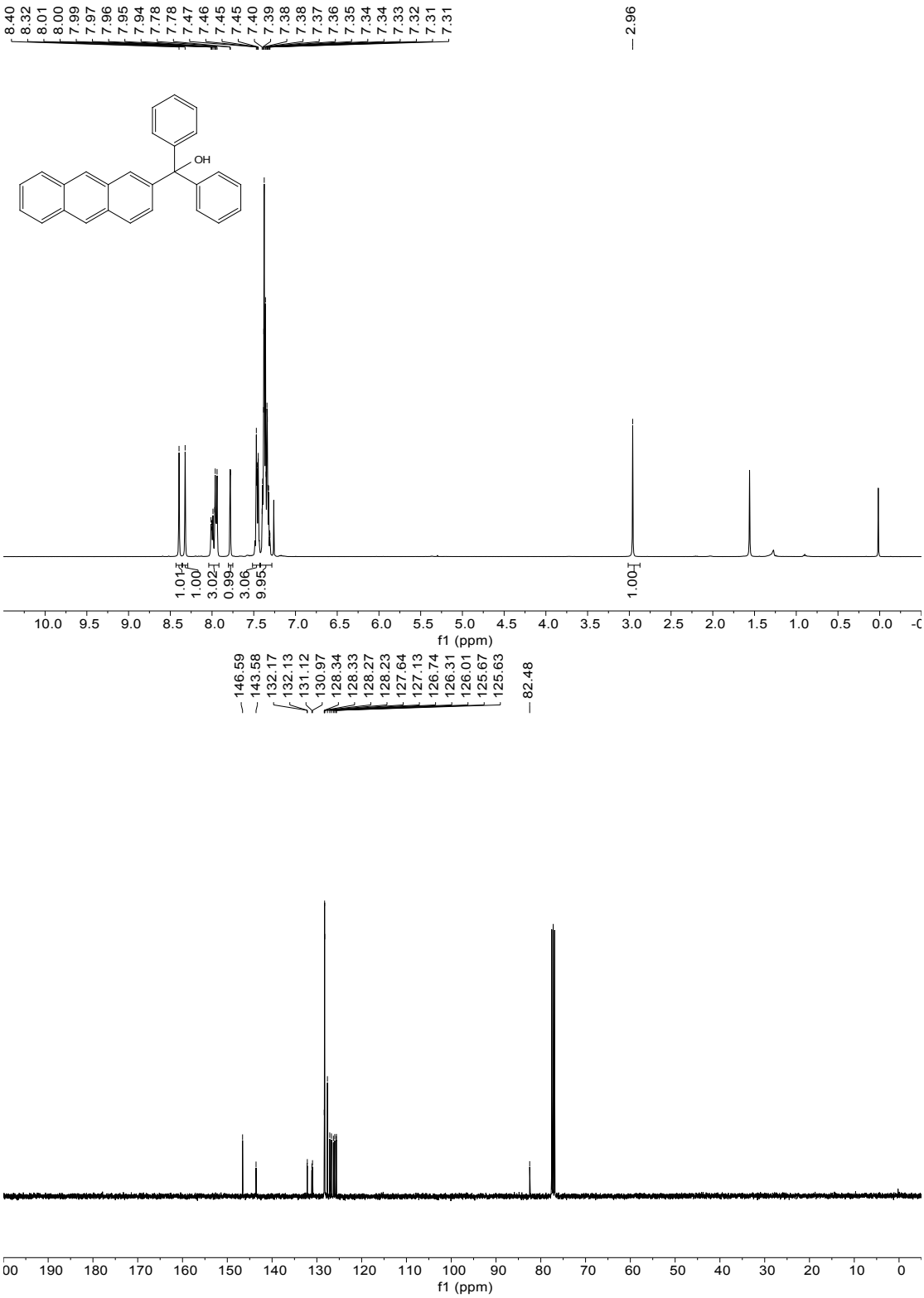


Fig. S10 ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of TAM-An in $CDCl_3$.

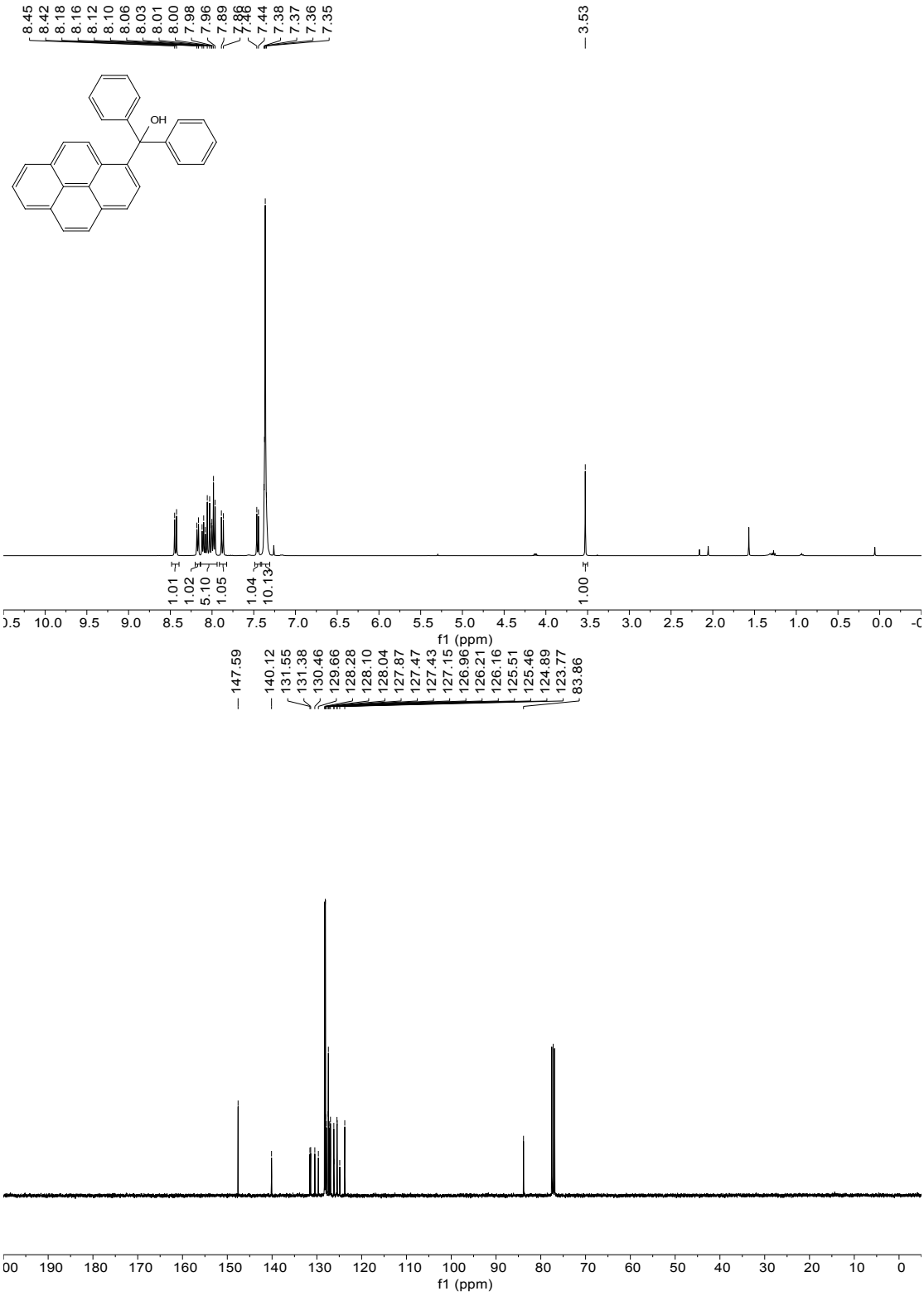


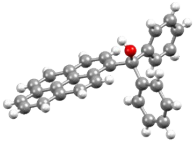
Fig. S11 ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of TAM-Py in $CDCl_3$.

Table S1 Results of energy-transfer efficiency and antenna effect.

Entry	ω (NiR)	Φ_{ET} (%)	Antenna Effect
1	**0.10**	**49.2**	**20.7**
2	**0.15**	**60.6**	**21.6**
3	**0.20**	**73.5**	**19.4**
4	**0.30**	**74.3**	**21.3**

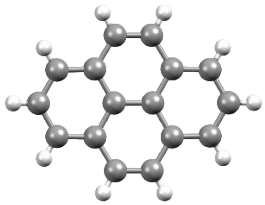
Single crystal data

Table S2 Crystal data and structure refinement for TAM-Py.



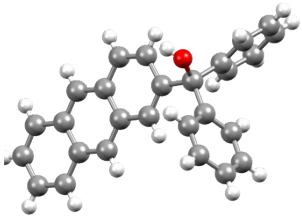
CCDC	1942288	
Identification code	TAM-Py	
Empirical formula	C29 H20 O	
Formula weight	384.45	
Temperature	211(12) K	
Wavelength	1.3405 Å	
Crystal system	Monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 13.7995(4) Å	α= 90°.
	b = 8.9671(3) Å	β= 90.297(3)°.
	c = 15.7683(5) Å	γ = 90°.
Volume	1951.17(11) $Å^3$	
Z	4	
Density (calculated)	1.309 Mg/m^3	
Absorption coefficient	0.385 mm^{-1}	
F(000)	808	
Crystal size	0.6 x 0.4 x 0.2 mm^3	
Theta range for data collection	2.784 to 60.583°.	
Index ranges	-17<=h<=17, -11<=k<=11, -17<=l<=20	
Reflections collected	15510	
Independent reflections	4347 [R(int) = 0.0265]	
Completeness to theta = 53.543°	99.9 %	
Absorption correction	Numerical	
Max. and min. transmission	1.00000 and 0.70221	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4347 / 0 / 276	
Goodness-of-fit on F^2	1.052	
Final R indices [I>2sigma(I)]	R1 = 0.0384, wR2 = 0.1005	
R indices (all data)	R1 = 0.0493, wR2 = 0.1077	
Extinction coefficient	0.0029(3)	
Largest diff. peak and hole	0.174 and -0.130 $e.Å^{-3}$	

Table S3 Crystal data and structure refinement for Pyrene.



CCDC	1942289	
Identification code	pyrene	
Empirical formula	C16 H10	
Formula weight	202.24	
Temperature	99.98(10) K	
Wavelength	1.3405 Å	
Crystal system	Monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 8.3726(3) Å	α= 90°.
	b = 9.1301(3) Å	β= 100.281(4)°.
	c = 13.5283(6) Å	γ = 90°.
Volume	1017.54(7) $Å^3$	
Z	4	
Density (calculated)	1.320 Mg/m^3	
Absorption coefficient	0.365 mm^{-1}	
F(000)	424	
Crystal size	0.6 x 0.4 x 0.2 mm^3	
Theta range for data collection	4.667 to 60.428°.	
Index ranges	-10<=h<=10, -11<=k<=11, -17<=l<=11	
Reflections collected	7374	
Independent reflections	2260 [R(int) = 0.0261]	
Completeness to theta = 53.543°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.63260	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2260 / 0 / 145	
Goodness-of-fit on F^2	1.081	
Final R indices [I>2sigma(I)]	R1 = 0.0408, wR2 = 0.1138	
R indices (all data)	R1 = 0.0530, wR2 = 0.1226	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.190 and -0.209 e.$Å^{-3}$	

Table S4 Crystal data and structure refinement for TAM-An.



CCDC	1985822	
Identification code	TAM-An	
Empirical formula	C27 H20 O	
Formula weight	360.43	
Temperature	253(6) K	
Wavelength	1.3405 Å	
Crystal system	Monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 11.6292(4) Å	α= 90°.
	b = 19.6591(6) Å	β= 99.289(3)°.
	c = 8.4982(3) Å	γ = 90°.
Volume	1917.38(11) $Å^3$	
Z	4	
Density (calculated)	1.249 Mg/m^3	
Absorption coefficient	0.368 mm^{-1}	
F(000)	760	
Crystal size	0.6 x 0.4 x 0.2 mm^3	
Theta range for data collection	3.348 to 60.461°.	
Index ranges	-15<=h<=14, -25<=k<=24, -11<=l<=10	
Reflections collected	13832	
Independent reflections	4270 [R(int) = 0.0271]	
Completeness to theta = 53.543°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.80650	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4270 / 0 / 258	
Goodness-of-fit on F^2	1.048	
Final R indices [I>2sigma(I)]	R1 = 0.0422, wR2 = 0.1081	
R indices (all data)	R1 = 0.0584, wR2 = 0.1176	
Extinction coefficient	0.0019(3)	
Largest diff. peak and hole	0.147 and -0.126 e.$Å^{-3}$	

Reference

1. Z. Xu, S. Peng, Y. Y. Wang, J. K. Zhang, A. I. Lazar and D. S. Guo, *Adv. Mater.*, 2016, **28**, 7666-7671.