

Supporting Information

Piezochromic fluorescence of anthracene derivative crystals with different stacking patterns designed around excimers

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Author Contributions

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Experimental details

Table S1

Fig. S1-S6

References

Experimental Section

All the reagents and solvents used for synthesis were purchased from Aldrich and Acros and used without further purification. ^1H and ^{13}C NMR spectra were recorded on a Bruker AVANCE 500 spectrometer, using tetramethylsilane (TMS) as the internal standard. The MALDI-TOF-MS mass spectra were recorded using an AXIMA-CFRTM plus instrument. The compounds were characterized by a Flash EA 1112, CHNS elemental analysis instrument. The synthetic details were shown in the Supporting Information.

Single crystal X-ray diffraction data

Single crystals of SA were collected by solvent diffusion method in dichloromethane-methanol system. Single crystals of TPA were grown according to a previous report.^[1] Single crystals of TPPA were grown according to a previous report.^[2] All single crystals were prepared at room temperature. The diffraction experiments were carried out on a Rigaku R-Axis RAPID diffractometer equipped with a Mo-K α and control Software using the RAPID AUTO at 293 (± 2) °C. The crystal structures were solved with direct methods and refined with a full-matrix least-squares technique using the SHELXS programs.

Photophysical measurements

Steady-state fluorescence spectra of SA, TPA, and TPPA in tetrahydrofuran (THF)-water mixed solutions were recorded using FLS980 Spectrometer. Time-resolved fluorescence spectra of crystals under ambient conditions were collected using time-correlated single photon counting (TSCPC) technique on a FLS980 Spectrometer.

High-pressure measurements

A 100- μm -diameter hole drilled in a pre-indented T301 stainless steel gasket was utilized as the sample chamber, which was placed in a symmetric diamond anvil cell (DAC). Pressure was measured using the standard ruby-fluorescence method.^[3] Silicon oil was used as the pressure-transmitting medium (PTM) for the high-pressure UV-Vis absorption and TPPA photoluminescence (PL) experiments. Argon was used as PTM in SA and TPA PL experiments to avoid silicon oil interference. All the high-pressure experiments were performed at room temperature. High-pressure UV-Vis absorption and PL were measured with an optical fiber spectrometer (Ocean Optics, QE6500) and the 355 nm line of UV DPSS laser with a power of 10 mW was used as the excitation source for PL measurements. In situ high-pressure time-resolved PL measurements were performed by a homemade microscope setup with a 375 nm pulsed diode laser (LDH-P-C-375B, 40 ps) as excitation source. A 20 \times ultraviolet objective lens was used to collect the backscattered emission signal after projecting the incident laser onto the sample by the 500 mm focal length grating spectrograph (HRS-500 MS, PI), with a time correlated single photon counting electronics (TimeHarp 260 PICO).

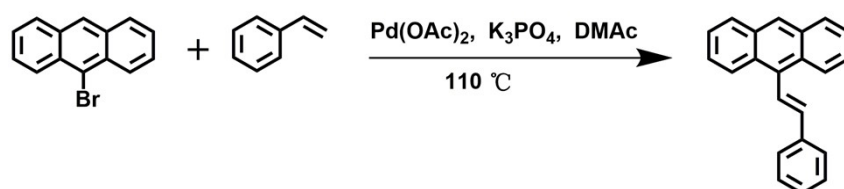
High-pressure geometric optimization

Ab initio calculations of the high-pressure crystal structure were performed by using the pseudopotential plane wave method in the CASTEP package.^[4] The generalized gradient approximation of Perdew-Burke-Ernzerh exchange correlation was used in the geometric optimization with a plane wave cutoff energy of 680 eV.^[5]

Theoretical calculation

Time-dependent density functional theory (TD-DFT) calculations were carried out for the natural transition orbitals (NTOs) at the level of B3LYP-GD3BJ/6-31G(d, p) using Gaussian 09 (version D.01) package on a Power Leader cluster.^[6] These theoretical calculations were carried out by taking initial coordinates from crystallographic data of single crystals and performed in gas phase.

Synthetic details



Scheme S1. Synthetic route to SA.

Synthesis of (E)-9-styrylanthracene (SA)

A mixture of 9-bromoanthracene (1.03 g, 4.00 mmol), styrene (1 mL, 8.70 mmol), Pd(OAc)₂ (26.94 mg, 0.12 mmol), K₃PO₄ (2.55 g, 12.00 mmol), and 20 mL *N,N*-dimethylacetamide (DMAc) was added in a 50 mL round-bottomed flask. It was degassed and recharged with nitrogen again. After the mixture was stirred and refluxed at 110 °C for 24 h under nitrogen atmosphere, 20 mL distilled water was added into this mixture and the final mixture was extracted with dichloromethane. The organic phase was dried with anhydrous sodium sulfate, filtered and concentrated in vacuum. It was purified via silica gel chromatography by petroleum ether to afford the desired compound in 27% yield (300 mg). m.p.: 130-133 °C; ¹H NMR (500 MHz, DMSO-*d*₆, 25 °C, TMS): δ = 8.59 (s, 1H, Ar-H), 8.39 – 8.34 (m, 2H, Ar-H), 8.14 (dd, *J* = 9.4, 6.3 Hz, 3H, Ar-H), 7.83 (d, *J* = 7.8 Hz, 2H, Ar-H), 7.56 (dd, *J* = 6.6, 3.0 Hz, 4H, Ar-H), 7.48 (t, *J* = 7.5 Hz, 2H, Ar-H), 7.38 (t, *J* = 7.4 Hz, 1H, CH), 6.98 (d, *J* = 16.9 Hz, 1H, CH); ¹³C NMR (125 MHz, CDCl₃, 25 °C, TMS): δ = 137.37 (C), 137.35 (CH), 132.81 (C), 131.55 (C), 129.78 (C), 128.88 (CH), 128.73 (CH), 128.06 (CH), 126.64 (CH), 126.50 (CH), 126.07 (CH), 125.50 (CH), 125.22 (CH), 124.92 (CH); MALDI-TOF MS (mass *m/z*): 280.48 [M⁺]; Anal. calcd for C₂₂H₁₆: C 94.25, H 5.75; found: C 94.42, H 5.88.

9-(1,2,2-triphenylvinyl)anthracene (TPA) was synthesized according to a previous report.^[1]

9-(4-(1,2,2-triphenylvinyl)phenyl)anthracene (TPPA) was synthesized according to a previous report.^[2]

Structural characterization

All the reagents and solvents used for the synthesis were purchased from Aldrich and Acros companies and used without further purification. ¹H and ¹³C NMR spectra were recorded on a Bruker AVANCE 500 spectrometer at 500 MHz, using tetramethylsilane (TMS) as the internal standard. The MALDI-TOF-MS mass spectra were recorded using an AXIMA-CFRM plus instrument. The compounds were characterized by a Flash EA 1112, CHNS elemental analysis instrument.

Table S1. Crystallographic data and refinement data of SA, TPA, and TPPA crystals.

	SA	TPA	TPPA
crystal color	yellow	colorless	colorless
empirical formula	C ₂₂ H ₁₆	C ₃₄ H ₂₄	C ₄₀ H ₂₈
formula weight	280.35	432.53	508.62
<i>T</i> [K]	293(2)	293(2)	293(2)
crystal system	monoclinic	orthorhombic	triclinic
space group	P 21/c	P bca	P -1
<i>a</i> [Å]	5.5188(11)	9.3706(3)	9.5948(6)
<i>b</i> [Å]	24.379(5)	19.2323(7)	9.7067(6)
<i>c</i> [Å]	11.411(2)	26.9687(10)	15.6253(11)
α [°]	90	90	79.680(3)
β [°]	100.06(3)	90	84.432(3)
γ [°]	90	90	84.978(3)
<i>V</i> [Å³]	1511.6(5)	4860.3(3)	1421.29(16)
<i>Z</i>	4	8	2
F(000)	592	1824	536
density [g/cm³]	1.232	1.182	1.188
μ [mm⁻¹]	0.070	0.067	0.067
reflections collected	13891	56061	24101
unique reflections	3361	6023	4996
<i>R</i> (int)	0.0372	0.0636	0.0535
GOF	1.065	1.055	1.026
<i>R</i>₁ [<i>I</i>>2σ(<i>I</i>)]	0.0540	0.0600	0.0525
ωR₂ [<i>I</i>>2σ(<i>I</i>)]	0.1634	0.1184	0.1066
<i>R</i>₁ (all data)	0.0760	0.1137	0.1067
ωR₂ (all data)	0.1825	0.1444	0.1341
CCDC number	2202296	1900042	1958726

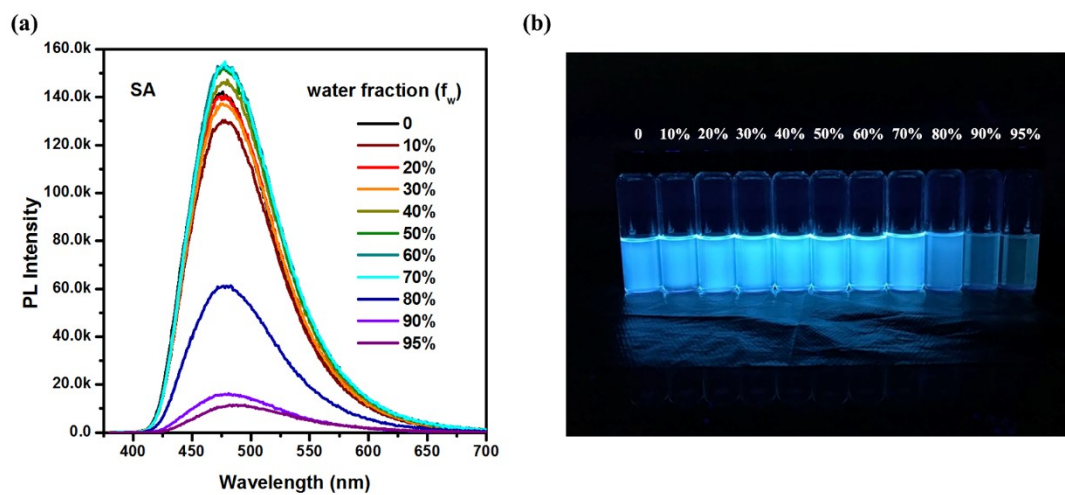


Fig. S1. (a) Emission spectra of SA in mixed water-THF solutions with various water fractions (f_w). (b) Photographs of SA in mixed water-THF solutions (the proportions of water are shown on the top) under 365 nm UV lamp irradiation.

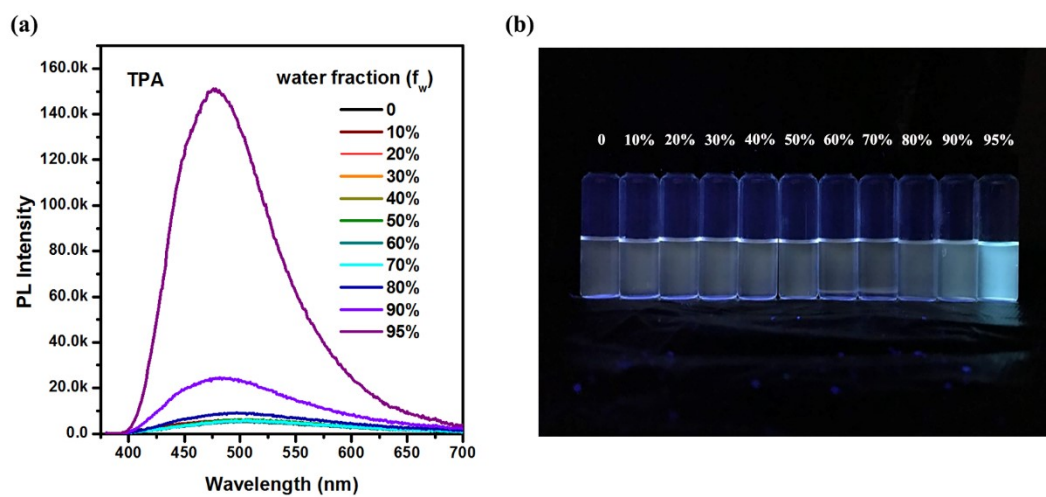


Fig. S2. (a) Emission spectra of TPA in mixed water-THF solutions with various water fractions (f_w). (b) Photographs of TPA in mixed water-THF solutions (the proportions of water are shown on the top) under 365 nm UV lamp irradiation.

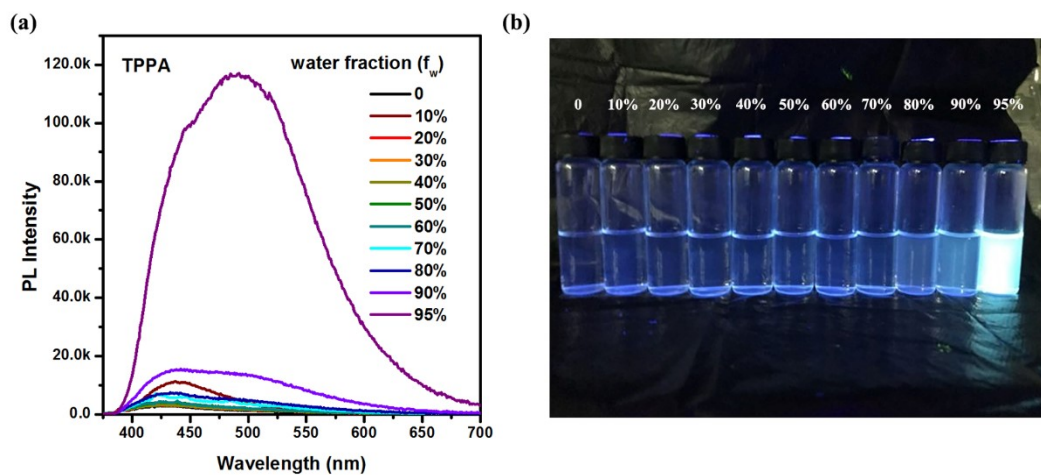


Fig. S3. (a) Emission spectra of TPPA in mixed water-THF solutions with various water fractions (f_w). (b) Photographs of TPPA in mixed water-THF solutions (the proportions of water are shown on the top) under 365 nm UV lamp irradiation.

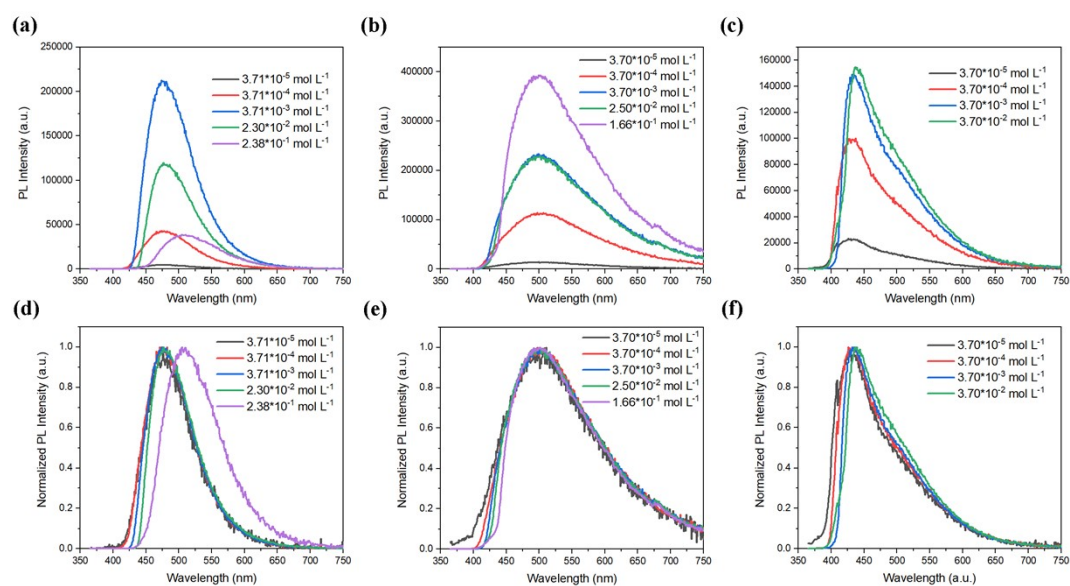


Fig. S4. Concentration-dependent PL spectra of (a) SA, (b) TPA, and (c) TPPA in chloroform solutions. Normalized concentration-dependent PL spectra of (d) SA, (e) TPA, and (f) TPPA in chloroform solutions.

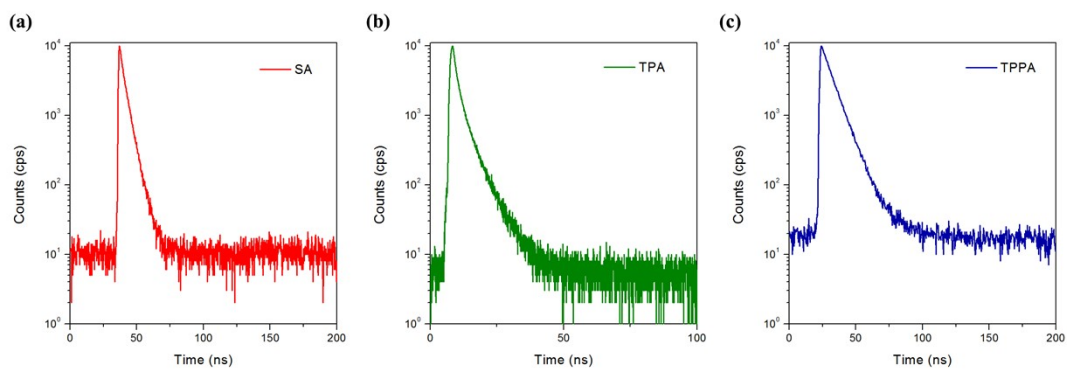


Fig. S5. Time-resolved PL spectra of (a) SA, (b) TPA, and (c) TPPA powder crystals under ambient conditions. (SA: 1.17 ns (18.52%), 4.22 ns (81.48%); TPA: 1.28 ns (50.47%), 4.66 ns (49.53%); TPPA: 2.69 ns (24.03%), 5.49 ns (75.97%))

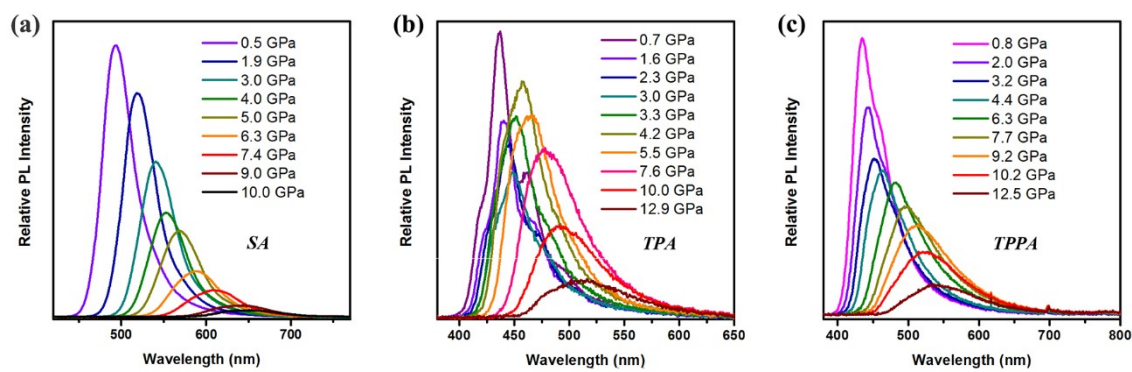


Fig. S6. (a) Fluorescent spectra of the SA crystal under the pressure from 0.5 to 10.0 GPa. (b) Fluorescent spectra of the TPA crystal under the pressure from 0.7 to 12.9 GPa. (c) Fluorescent spectra of the TPPA crystal under the pressure from 0.8 to 12.5 GPa.

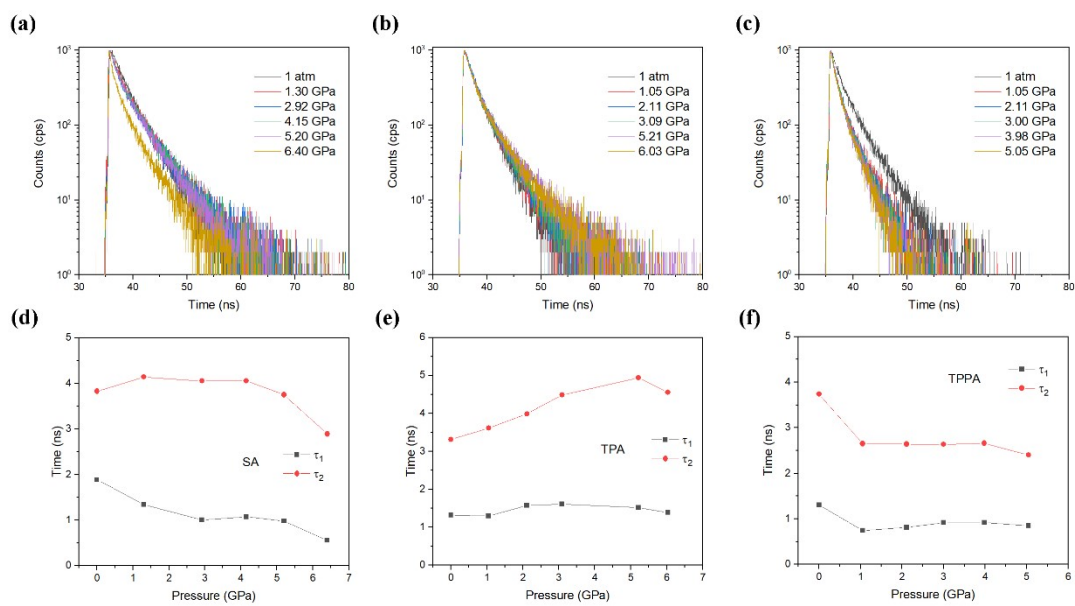


Fig. S7. Time-resolved PL spectra of (a) SA, (b) TPA, and (c) TPPA crystals under different pressures. Plot of lifetime against pressure for (d) SA, (e) TPA, and (f) TPPA.

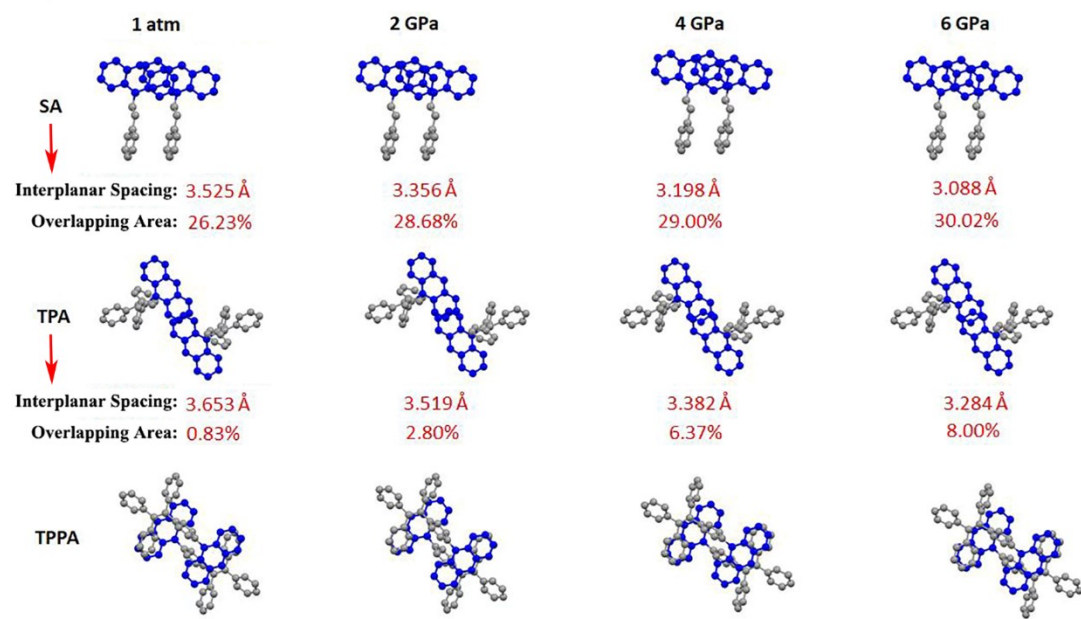


Fig. S8. The aggregation evolution of SA, TPA and TPPA molecules during the pressurization by geometry optimization. The interplanar spacing and overlapping area of anthracene units in SA and TPA molecules are identified.

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