

## Supporting Information

### A Comparative Investigation on Excimer Fluorescence Toward Its Bright Future

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## SI Materials and experimental methods

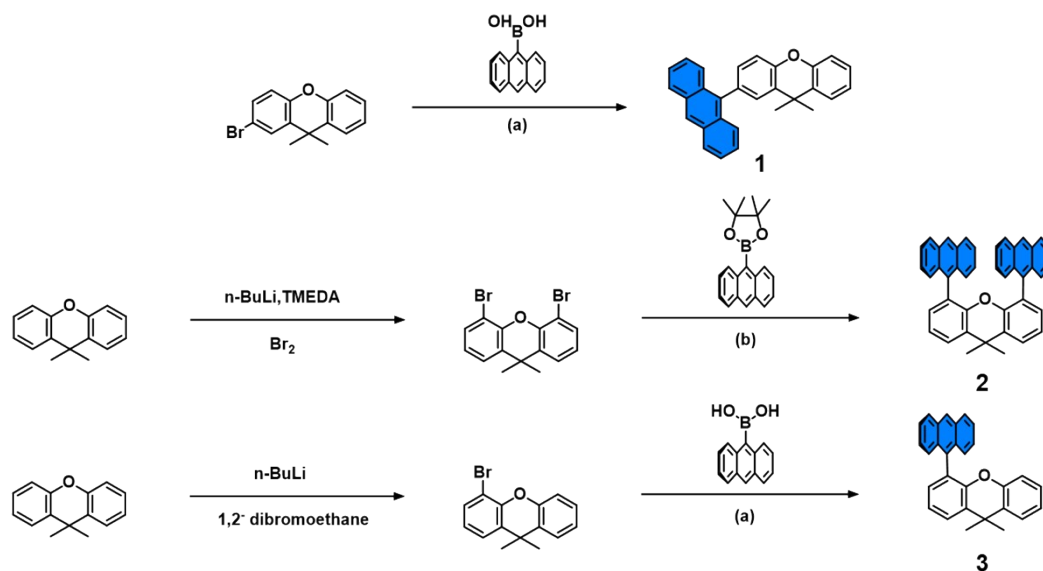
**General information:** All the reagents and solvents used for the synthesis were purchased from Aldrich and Acros companies and used without further purification. The  $^1\text{H}$  NMR data were recorded on a Bruker AVANCE 500 spectrometer at 500 MHz.  $\text{CD}_2\text{Cl}_2$  and  $\text{CDCl}_3$  were selected as solvents for  $^1\text{H}$  NMR. The mass spectra (MS) were recorded using an ITQ1100 (Thermo Fisher). The compounds were characterized by a Vario MICRO cube CHNS elemental analysis instrument.

**Spectroscopy measurements:** UV-vis spectra of solutions were recorded on a Shimadzu UV-3100 Spectrophotometer. Steady-state photoluminescence (PL) spectra, time-resolved PL spectra and temperature-dependent PL spectra were carried out by FLS980 Fluorescence Spectrometer by Edinburgh Instruments. Photoluminescence quantum yields (PLQYs) were measured using an integrating sphere apparatus. The  $k_r$  and  $k_{nr}$  are estimated on the basis of the known PLQY and lifetime according to the following formulas:  $k_r = \text{PLQY}/\tau$ ,  $k_{nr} = 1/\tau - k_r$ .

**X-ray diffraction (XRD):** Single crystals of **1**, and **2** were cultivated by slow solvent diffusion method in dichloromethane (DCM) /methanol systems. The diffraction experiments of **1** and **2** crystals were carried out on a Rigaku R-AXIS RAPID diffractometer equipped with a Mo-K $\alpha$  and control Software using the RAPID AUTO. The crystal structures were solved with direct methods and refined with a full-matrix least-squares technique using the Olex2 programs.

**Theoretical calculation:** All the density functional theory (DFT) calculations were carried out using Gaussian 16 (version D.01) package<sup>[1]</sup> on a Power Leader cluster. Time-dependent DFT (TD-DFT) calculations were carried out for the natural transition orbitals (NTOs) and geometry optimization at the level of M06-2X /6-31G(d, p). The transition density matrix (TDM) maps were obtained using Multiwfn program (version 3.8).<sup>[2]</sup> The charge transfer (CT) content was evaluated by following formula:  $R_{\text{CT}} = M_{\text{CT}}/M_{\text{TOTAL}}$  ( $R_{\text{CT}}$  represents the ratios of CT in certain excited state;  $M_{\text{CT}}$  and  $M_{\text{TOTAL}}$  represent the sum of the matrix elements in CT areas and total areas, respectively).

## SII Synthetic details



**Scheme S1.** Synthetic routes to 2-(anthracen-9-yl)-9,9-dimethyl-9H-xanthene (**1**), 4,5-di(anthracen-9-yl)-9,9-dimethyl-9H-xanthene (**2**), 4-(anthracen-9-yl)-9,9-dimethyl-9H-xanthene, and (**3**), 4,5-di(anthracen-9-yl)-2,7-di-*tert*-butyl-9,9-dimethyl-9H-xanthene compounds. Conditions: (a)  $K_2CO_3$ ,  $Pd(PPh_3)_4$ , toluene, deionized water, tetrahydrofuran,  $90^\circ C$ , 48h (b)  $K_2CO_3$ , Bis (di-*tert*-butyl(4-dimethylaminophenyl) phosphine) dichloropalladium (II) (887919-35-9), tetrahydrofuran, deionized water, reflux, 48 h.

### Synthesis of **1**

A mixture of anthracen-9-ylboronic acid (1 g, 4.5 mmol), 2-bromo-9,9-dimethyl-9H-xanthene (596 mg, 2 mmol),  $K_2CO_3$  (3 g, 21.7 mmol), 12 mL toluene, 8 mL distilled water and 6 mL tetrahydrofuran was degassed and recharged with nitrogen. Then  $Pd(PPh_3)_4$  (92 mg, 0.08 mmol) was added in the mixture as catalyst, and the mixture was degassed and recharged with nitrogen again. After stirred and refluxed at  $90^\circ C$  for 48 h under nitrogen atmosphere, the mixture was extracted with dichloromethane (DCM). The organic phase was dried with anhydrous sodium sulfate, filtered and concentrated in vacuum. It was purified via silica gel chromatography by the mixture of petroleum ether/dichloromethane (10:1) and then sublimation to afford the white powder in 71% yield (548 mg).  $^1H$  NMR (500 MHz, Methylene Chloride- $d_2$ , TMS,  $25^\circ C$ ):  $\delta$  = 8.56 (s, 1H, Ar-H), 8.11 (d, J =

8.5 Hz, 2H, Ar-H), 7.77 (m, 2H, Ar-H), 7.56 – 7.48 (m, 4H, Ar-H), 7.41 (m, 2H, Ar-H), 7.34 – 7.27 (m, 3H, Ar-H), 7.21 – 7.14 (m, 2H, Ar-H), 1.71 (s, 6H, CH<sub>3</sub>). GC/MS, EI (mass m/z): 386.35. Anal. calcd for C<sub>51</sub>H<sub>46</sub>O: C 90.12, H 5.74; found: C 90.64, H 5.84.

### Synthesis of 4,5-dibromo-9,9-dimethyl-9H-xanthene

The synthesis of 4,5-dibromo-9,9-dimethyl-9H-xanthene refers to Ref. S3.<sup>[3]</sup> 9,9-Dimethylxanthene (4.8 mmol, 1.0 g), TMEDA (14 mmol, 2.09 mL), and ethyl ether (45 mL) were cooled to -78 °C. A 2.5 M solution of n-butyllithium in hexane (14 mmol, 5.6 mL) was added, and the reaction mixture was stirred at room temperature for 20 h. A solution of bromine (1mL) in hexane (10 mL) was added dropwise at -78 °C, after which the reaction mixture was allowed to warm to room temperature overnight. Then a 20% aqueous solution of sodium sulphite was added. The organic phase was separated, and the aqueous phase was washed with DCM. The organic phase was dried with anhydrous sodium sulfate, filtered and concentrated in vacuum. It was purified via silica gel chromatography by the mixture of petroleum ether to afford the yellow oil. <sup>1</sup>H NMR (500 MHz, Chloroform-*d*, TMS, 25 °C): δ = 7.51 (m, 2H, Ar-H), 7.38 (m, 2H, Ar-H), 7.02 (t, *J* = 7.9 Hz, 2H, Ar-H), 1.65 (s, 6H, CH<sub>3</sub>). GC/MS, EI (mass m/z): 369.45

### Synthesis of 2

The synthesis of 2 refers to Ref. S4.<sup>[4]</sup> A mixture of anthracen-9-ylboronic acid (1.8 g, 8 mmol), 4,5-dibromo-9,9-dimethyl-9H-xanthene (736 mg, 2 mmol), K<sub>2</sub>CO<sub>3</sub> (1.1 g, 8 mmol), and 40 ml tetrahydrofuran was degassed and recharged with nitrogen. Then Bis(di-tert-butyl (4-dimethylaminophenyl) phosphine) dichloropalladium (II) (100 mg, 0.14 mmol) was added in the mixture as catalyst, and the mixture was degassed and recharged with nitrogen again. After stirred and refluxed for 24 h under nitrogen atmosphere, the mixture was extracted with dichloromethane (DCM). The organic phase was dried with anhydrous sodium sulfate, filtered and concentrated in vacuum. It was purified via silica gel chromatography by the mixture of petroleum ether/dichloromethane (10:1) and then sublimation to afford the white powder in 32% yield (360 mg). <sup>1</sup>H NMR (500 MHz, Methylene Chloride-*d*<sub>2</sub>, TMS, 25 °C): δ = 7.96 (s, 2H, Ar-H), 7.69 – 7.61 (m, 6H, Ar-H), 7.22 (t, *J* = 7.6 Hz, 2H, Ar-H), 7.07 – 6.97 (m, 8H, Ar-H), 6.96 (d, *J* = 1.6 Hz, 2H,

Ar-H), 6.78 (m, 4H, Ar-H), 1.93 (s, 6H, CH<sub>3</sub>). GC/MS, EI (mass m/z): 562.10. Anal. calcd for C<sub>51</sub>H<sub>46</sub>O: C 91.78, H 5.37; found: C 91.42, H 5.53.

### Synthesis of 4-bromo-9,9-dimethyl-9H-xanthene

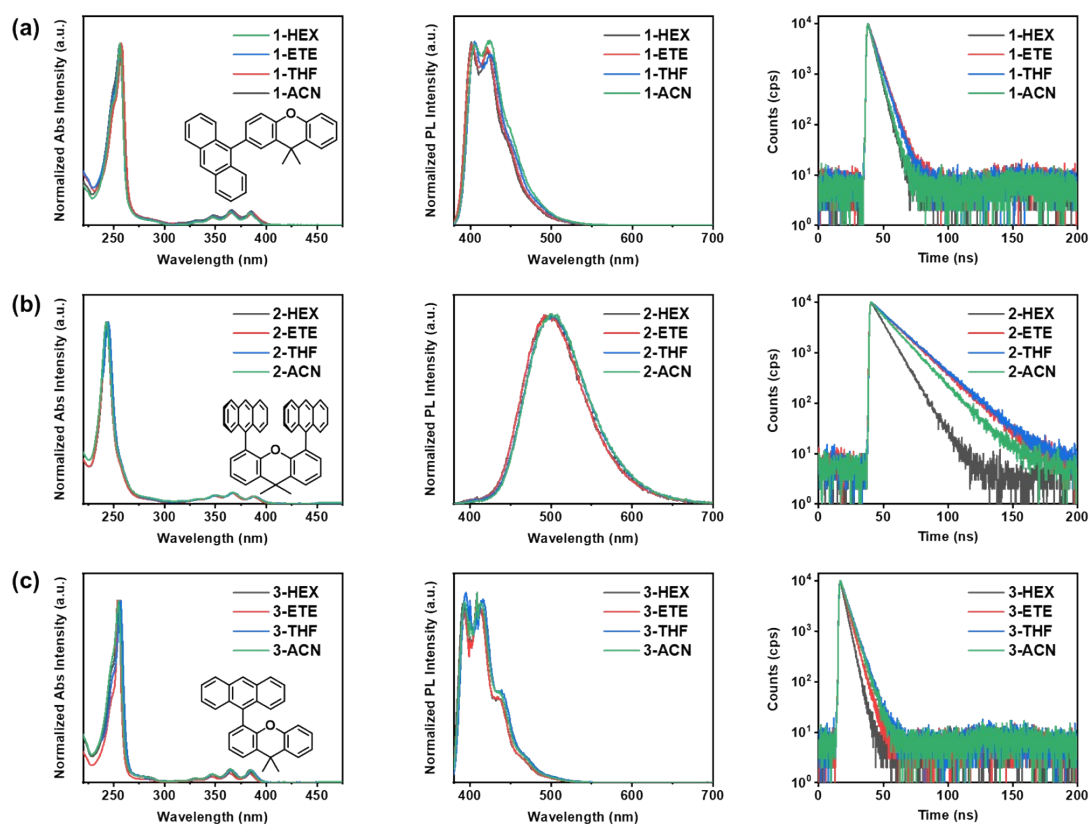
The synthesis of 4-bromo-9,9-dimethyl-9H-xanthene refers to Ref. S5.<sup>[5]</sup> 9,9'-Di-methylxanthene (4.8 mmol, 1.0 g), and dehydrated THF (10 mL) were cooled to -78 °C. A 2.5 M solution of n-butyllithium in hexane (5 mmol, 2 mL) was added, and the reaction mixture was stirred for 5 hours the temperature was raised to room temperature. After the reaction solution was cooled again to -78 °C, 1,2-dibromoethane (0.83 mL) was added slowly and stirred for 2 hours then warmed to room temperature. Water was added to stop the reaction, the organic layer was extracted with DCM. The organic phase was dried with anhydrous sodium sulfate, filtered and concentrated in vacuum. It was purified via silica gel chromatography by the mixture of petroleum ether to afford the yellow oil. GC/MS, EI (mass m/z): 287.84.

### Synthesis of 3

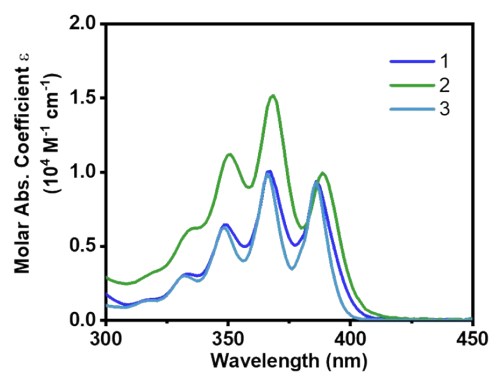
The synthesis of **3** is similar as **1** except the 4-bromo-9,9-dimethyl-9H-xanthene was used. <sup>1</sup>H NMR (500 MHz, Methylene Chloride-*d*<sub>2</sub>, TMS, 25 °C): δ = 8.61 (s, 1H, Ar-H), 8.14 (d, *J* = 8.5 Hz, 2H, Ar-H), 7.72 (m, 1H, Ar-H), 7.67 (m, 2H, Ar-H), 7.55 – 7.46 (m, 3H, Ar-H), 7.42 – 7.33 (m, 3H, Ar-H), 7.25 (m, 1H, Ar-H), 7.06 (m, 1H, Ar-H), 6.98 (m, 1H, Ar-H), 6.26 (m, 1H, Ar-H), 1.79 (s, 6H, CH<sub>3</sub>). GC/MS, EI (mass m/z): 386.11. Anal. calcd for C<sub>51</sub>H<sub>46</sub>O: C 90.12, H 5.74; found: C 90.58, H 5.82.

## SIII Figures and tables

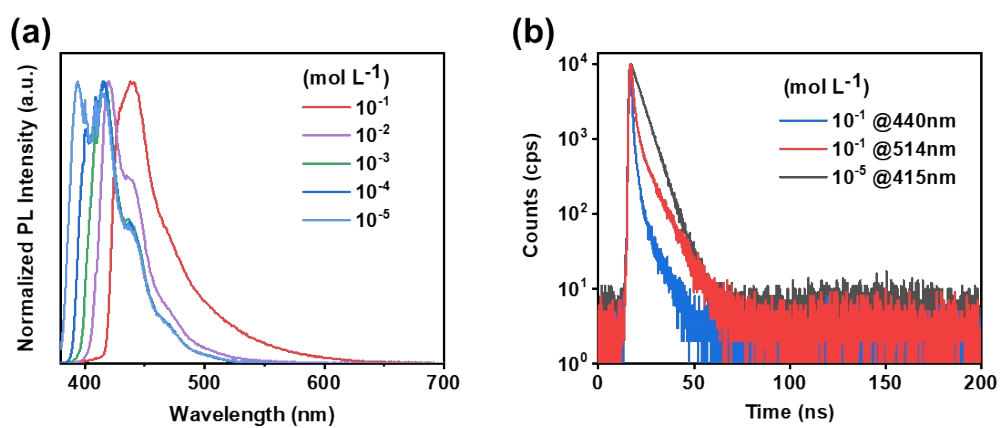
### Photophysical properties in dynamic environment



**Fig. S1.** UV-Vis spectra, PL spectra, and time-resolved PL spectra of (a) **1**, (b) **2**, and (c) **3** in different diluted solutions ( $10^{-5}$  mol L $^{-1}$ ) (HEX: hexane, ETE: ethyl ether, THF: tetrahydrofuran, ACN: acetonitrile).

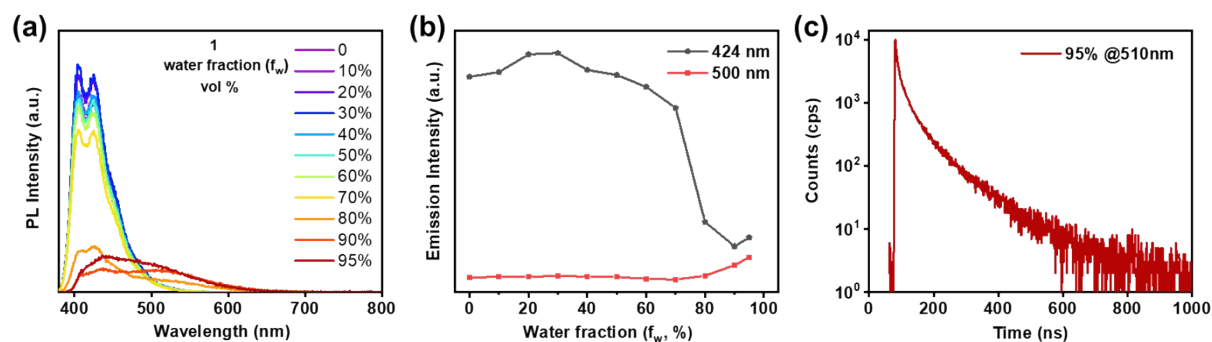


**Fig. S2.** Molar absorption coefficient of **1**, **2**, and **3**.

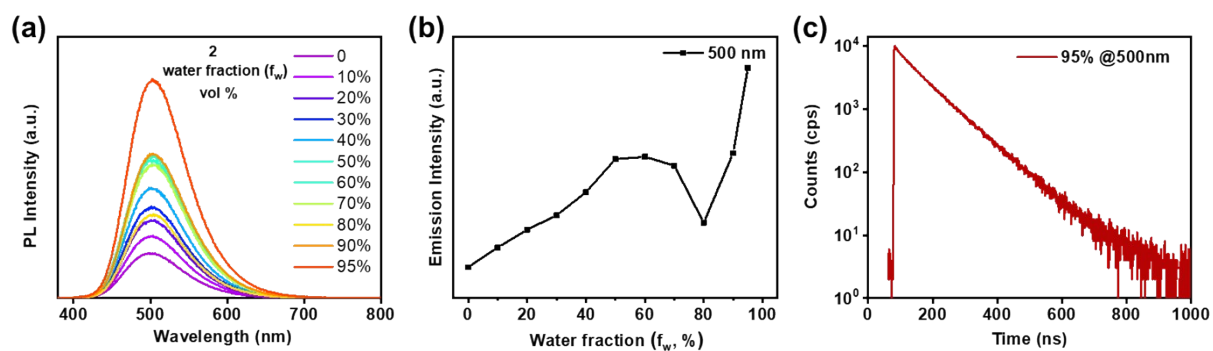


**Fig. S3.** (a) Concentration-dependent PL spectra of **3**. (b) Time-resolved PL spectra of **3** in THF solutions with various concentrations. From PL spectra and time-resolved PL spectra, **3** does not exhibit the excimer emission characters like **1**.



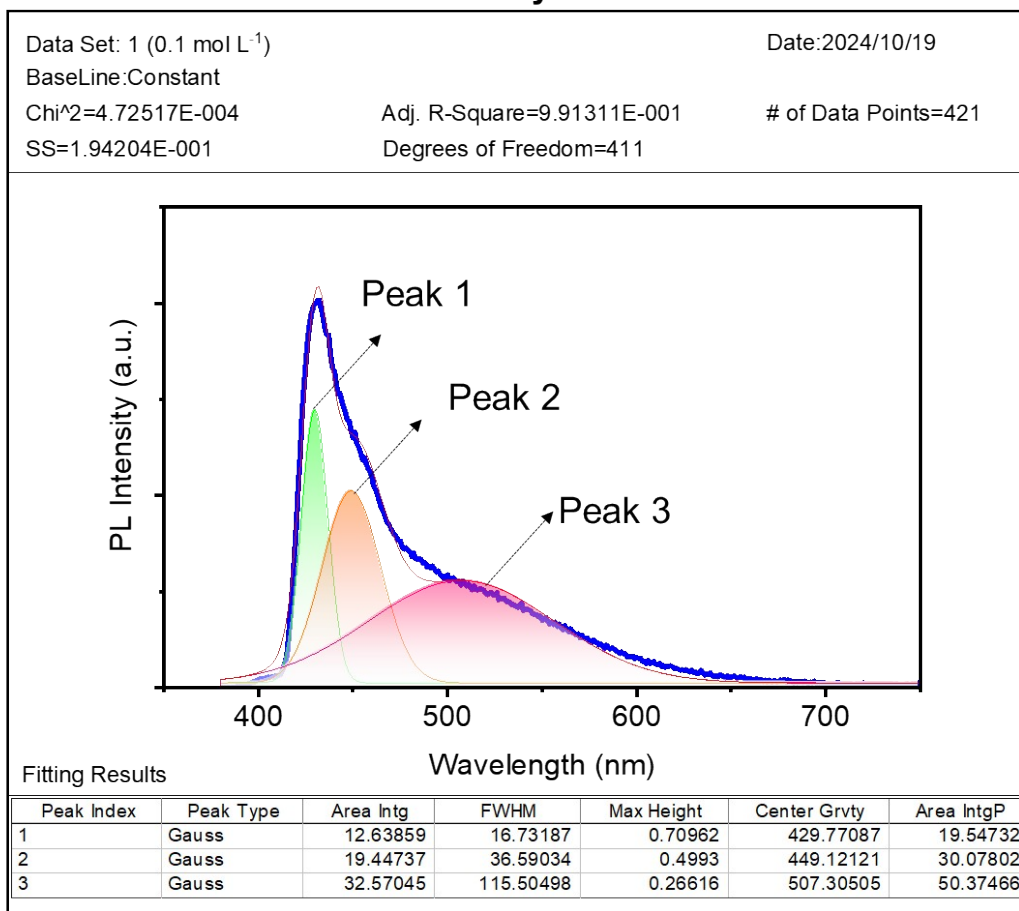


**Fig. S4.** (a) PL spectra, (b) emission intensity vs. water fraction ( $f_w$ ) vol % in THF and (c) time-resolved PL spectra of **1** in mixed THF:H<sub>2</sub>O solvents.



**Fig. S5** (a) PL spectra, (b) emission intensity vs. water fraction ( $f_w$ ) vol % in THF and (c) time-resolved PL spectra of **2** in mixed THF:H<sub>2</sub>O solvents.

## Peak Analysis



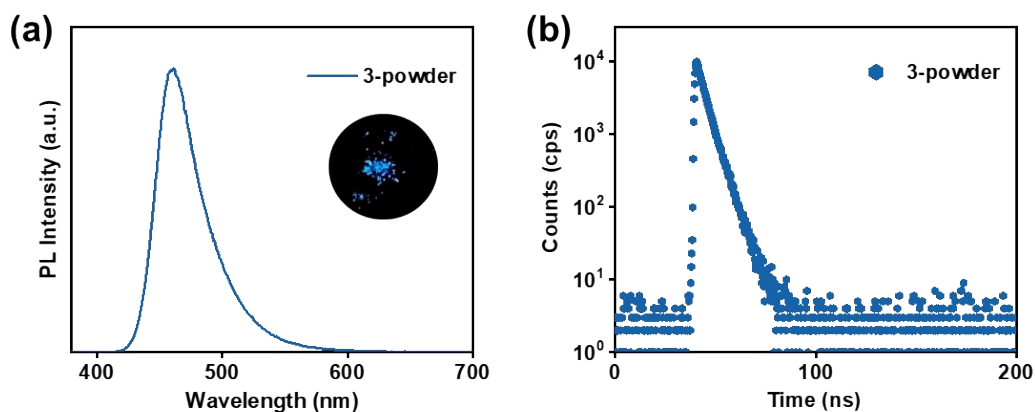
**Fig. S6.** Peak fitting analysis of emission spectrum of the high-concentration solution (10<sup>-1</sup> mol L<sup>-1</sup>) of **1**.

**Table S1.** The photophysics data of **1** and **2** in THF solution (dynamic environment).

		$\lambda_{\text{em}}$ (nm)	$\tau$ (ns)	PLQY (%)	$k_r$ ( $10^6 \text{ s}^{-1}$ )	$k_{\text{nr}}$ ( $10^6 \text{ s}^{-1}$ )
<b>1</b> in solution	monomer	405	5.28	47.04	89.1	100
	excimer	514	15.63	6.01	3.85	60.1
<b>2</b> in solution	monomer	395	5.46	43.15	79.0	104
	excimer	500	18.69	12.86	6.88	46.6

### Photophysical properties in static environment

We have tried our efforts to grow crystals of molecule **3** using the different solvent diffusion or vapor deposition method. Unfortunately, we could not obtain the crystals of molecule **3**. PL spectra and time-resolved PL spectra of pristine **3** solid powder were shown in **Fig. S7**, which did not exhibit the excimer emission characters.



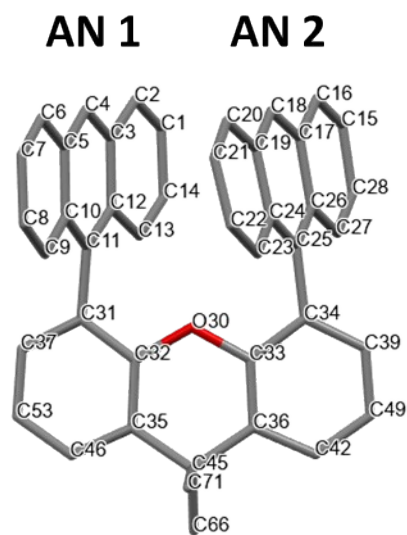
**Fig. S7.** (a) PL spectra and (b) time-resolved PL spectra of pristine **3** powder. The pristine powders of **3** emit around 460 nm with a lifetime of 4.47 ns, which does not exhibit the excimer emission.

**Table S2.** The individual lifetime components of **1** and **2** crystals.

	$\tau_1$ / Rel%	$\tau_2$ / Rel%	$\tau$ (ns) <sup>a</sup>
1	152.7 ns	-	152.7 ns
2	16.45 ns / 24.20%	47.99 ns / 75.80%	40.36 ns

<sup>a</sup> The average lifetimes are estimated on the basis of the following formula:  $\tau = \tau_1 \times \text{Rel}\% + \tau_2 \times \text{Rel}\%$ .

Single crystal conformation



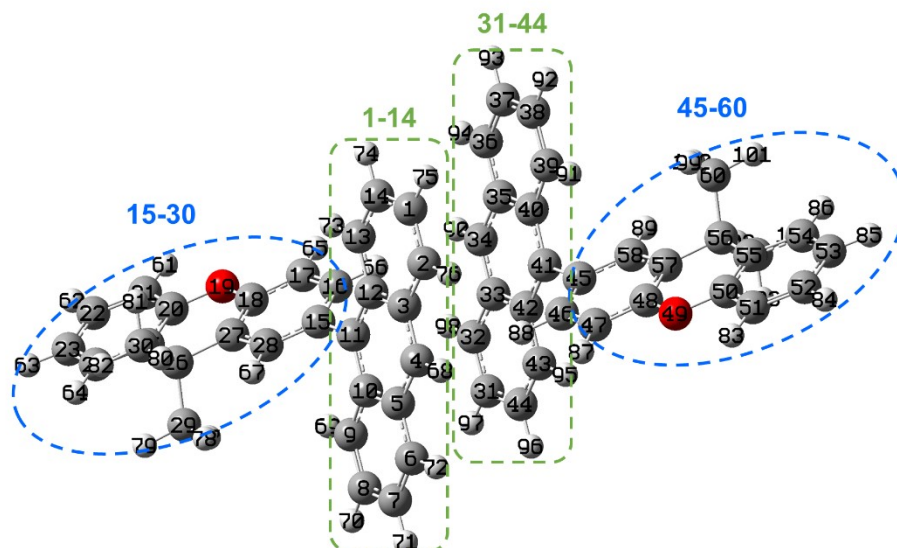
**Fig. S8.** Atom labels of molecule 2 configuration.

**Table S3.** Perpendicular distances between the AN 1 plane and the AN 2 plane C15–28 atoms as well as between the AN 2 plane with the AN 1 plane C1–14 atoms in **2** crystal. Atomic number is shown in **Fig. S8**.

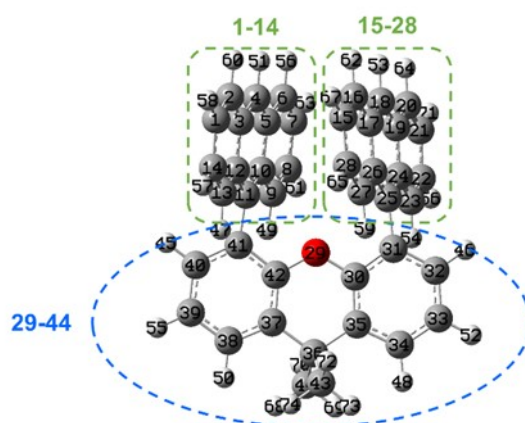
AN 1	Å	AN 2	Å
C15	3.470	C1	3.359
C16	3.414	C2	3.353
C17	3.543	C3	3.559
C18	3.448	C4	3.505
C19	3.604	C5	3.643
C20	3.509	C6	3.545
C21	3.709	C7	3.666
C22	4.031	C8	3.885
C23	4.113	C9	4.000
C24	3.882	C10	3.898
C25	3.918	C11	4.032
C26	3.757	C12	3.818
C27	3.772	C13	3.820
C28	3.642	C14	3.582
average <sup>a</sup>	3.701	average <sup>a</sup>	3.690

<sup>a</sup> As two AN planes within a dimer are unparallel, the average distance was determined to be the average perpendicular distance between one AN plane and carbon atoms of the other AN plane. The shorter average distance (3.690 Å) was used in the main text.

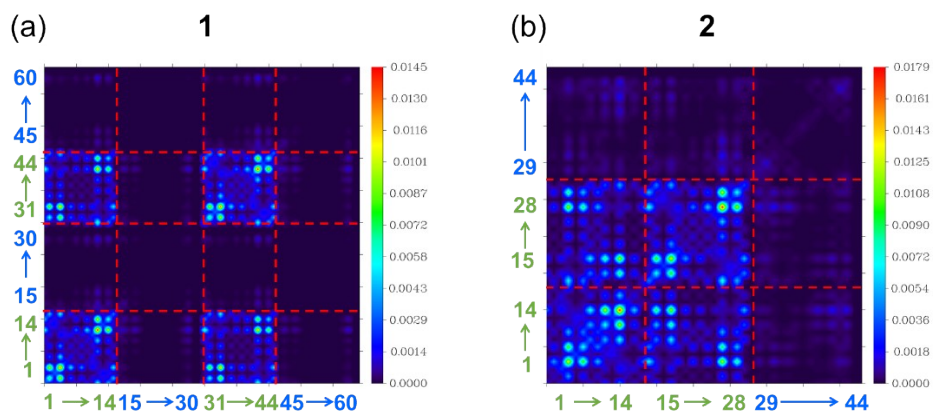
## Theoretical calculation



**Fig. S9.** Labeled atoms for the calculation of TDM map of **1** dimer. All non-hydrogen atoms are assigned a sequence number in fragment order. Since hydrogen atoms usually have little contribution to the transitions we are interested in, they are usually ignored by default.



**Fig. S10.** Labeled atoms for the calculation of TDM map of **2** dimer.



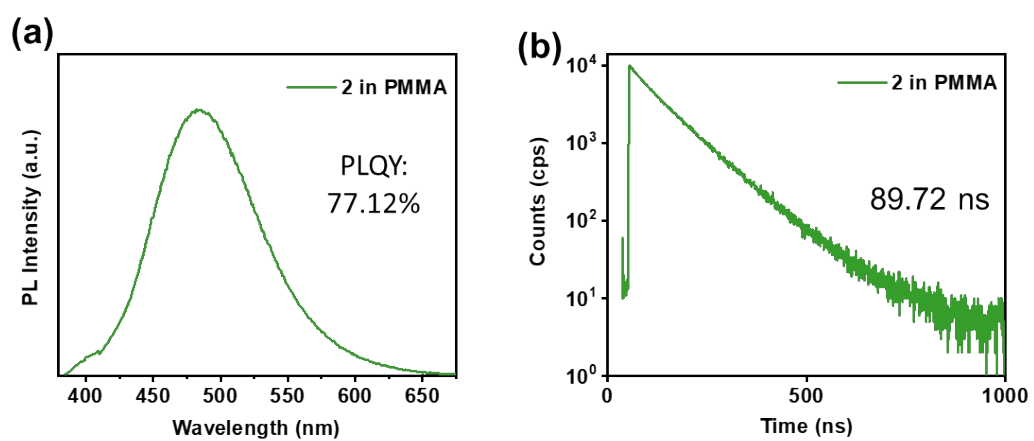
**Fig. S11.** TDM color-filled maps of the  $S_1$  state for (a) **1** dimer and (b) **2** dimer.

It can be found that the brightest zones are concentrated along the diagonal and off-diagonal, indicating a strong state interaction between two AN units, which can be ascribed to the excited state nature of hybridized local and charge-transfer state (HLCT): two diagonal parts are the LE transition of two AN units, off-diagonal parts are the CT transition from one AN unit to another. Furthermore, the CT contents of two dimers in the  $S_1$  excited state can be evaluated according to the matrix elements by following formulas:  $R_{CT} = M_{CT}/M_{TOTAL}$  ( $R_{CT}$  represents the ratios of CT in certain excited state;  $M_{CT}$  and  $M_{TOTAL}$  represent the sum of the matrix elements in CT areas and total areas, respectively).

**Table S4.** The CT contents of **1** dimer and **2** dimer in the  $S_1$  state.

	CT content
<b>1</b>	0.380
<b>2</b>	0.343





**Fig. S12.** (a) PL spectra and (b) time-resolved PL spectra of 1% weight percent **2** doped in polymethyl methacrylate (PMMA) film.

## Crystallographic data

**Table S5.** Crystallographic data and refinement data of **1** and **2** crystals.

	<b>1</b>	<b>2</b>
<b>crystal color</b>	yellow	yellow
<b>empirical formula</b>	C <sub>29</sub> H <sub>22</sub> O	C <sub>43</sub> H <sub>30</sub> O
<b>formula weight</b>	386.50	562.67
<b>T [K]</b>	273	302
<b>crystal system</b>	monoclinic	triclinic
<b>space group</b>	C2 /c	P-1
<b>a [Å]</b>	26.9512(10)	9.1255(5)
<b>b [Å]</b>	9.4305(3)	17.9972(11)
<b>c [Å]</b>	17.3290(6)	18.3091(11)
<b>α [°]</b>	90	90.153(2)
<b>β [°]</b>	111.921(1)	90.817(2)
<b>γ [°]</b>	90	94.909(2)
<b>V [Å<sup>3</sup>]</b>	4086.0(3)	2995.6(3)
<b>Z</b>	8	4
<b>F(000)</b>	1632	1184
<b>density [g/cm<sup>3</sup>]</b>	1.257	1.248
<b>μ [mm<sup>-1</sup>]</b>	0.074	0.073
<b>reflections collected</b>	41813	168041
<b>unique reflections</b>	4703	13770
<b>R (int)</b>	0.0543	0.0348
<b>GOF</b>	1.288	1.055
<b>R<sub>1</sub> [I&gt;2σ(I)]</b>	0.0573	0.0517
<b>ωR<sub>2</sub> [I&gt;2σ(I)]</b>	0.1520	0.1280
<b>R<sub>1</sub> (all data)</b>	0.0980	0.0709
<b>ωR<sub>2</sub> (all data)</b>	0.2013	0.1518
<b>CCDC number</b>	2376432	2404819

## SIV Reference

- [1] Gaussian 16, Revision A.03, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.
- [2] T. Lu and F. Chen, *J. Comput. Chem.*, **2012**, 33, 580-592.
- [3] A. Buhling, P. C. J. Kamer, P. W. N. M. van Leeuwen, J. W. Elgersma, K. Goubitz, J. Fraanje, *Organometallics* **1997**, 16, 3027-3037.
- [4]. Q. Liao, A. Li, A. Huang, J. Wang, K. Chang, H. Li, P. Yao, C. Zhong, P. Xie, J. Wang, Z. Li, Q. Li, *Chem. Sci.* **2024**, 15, 4364-4373.
- [5] Jpn. Pat., JP6023635B2, 2016.