

## Supporting Information

### Bis(tricyclic) Aromatic Enes That Exhibit Efficient Fluorescence in the Solid State

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$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of 2a, 3a, and 3c

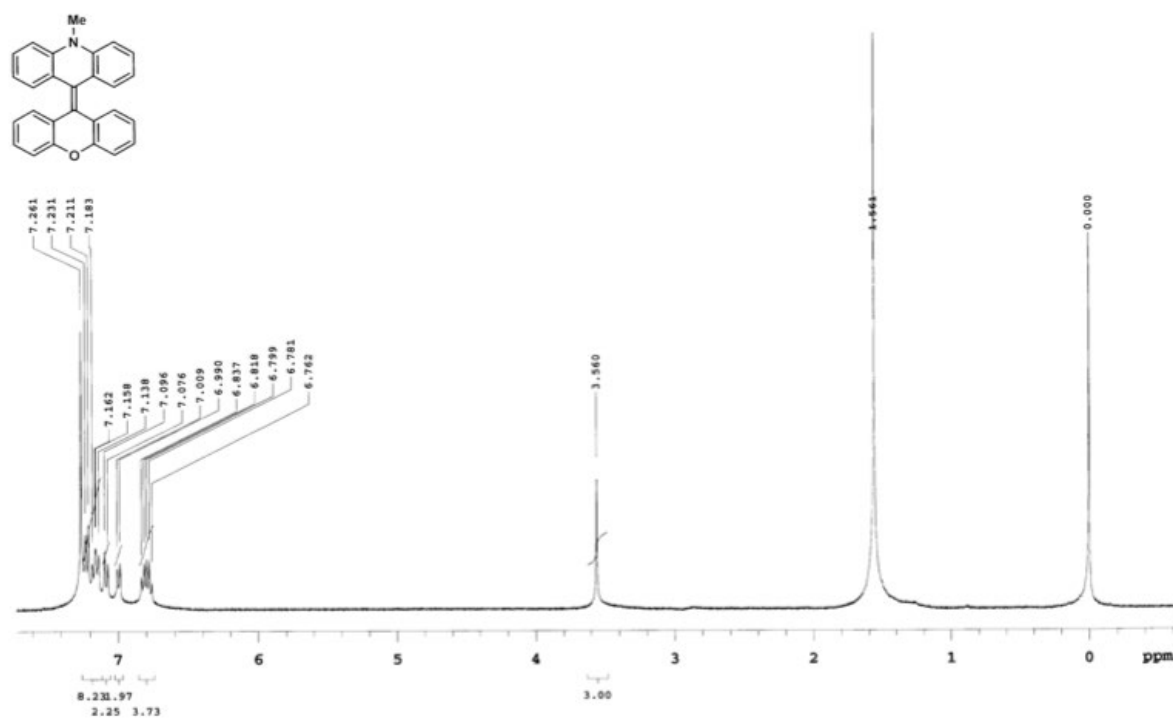


Figure S1.  $^1\text{H}$  NMR of 2a.

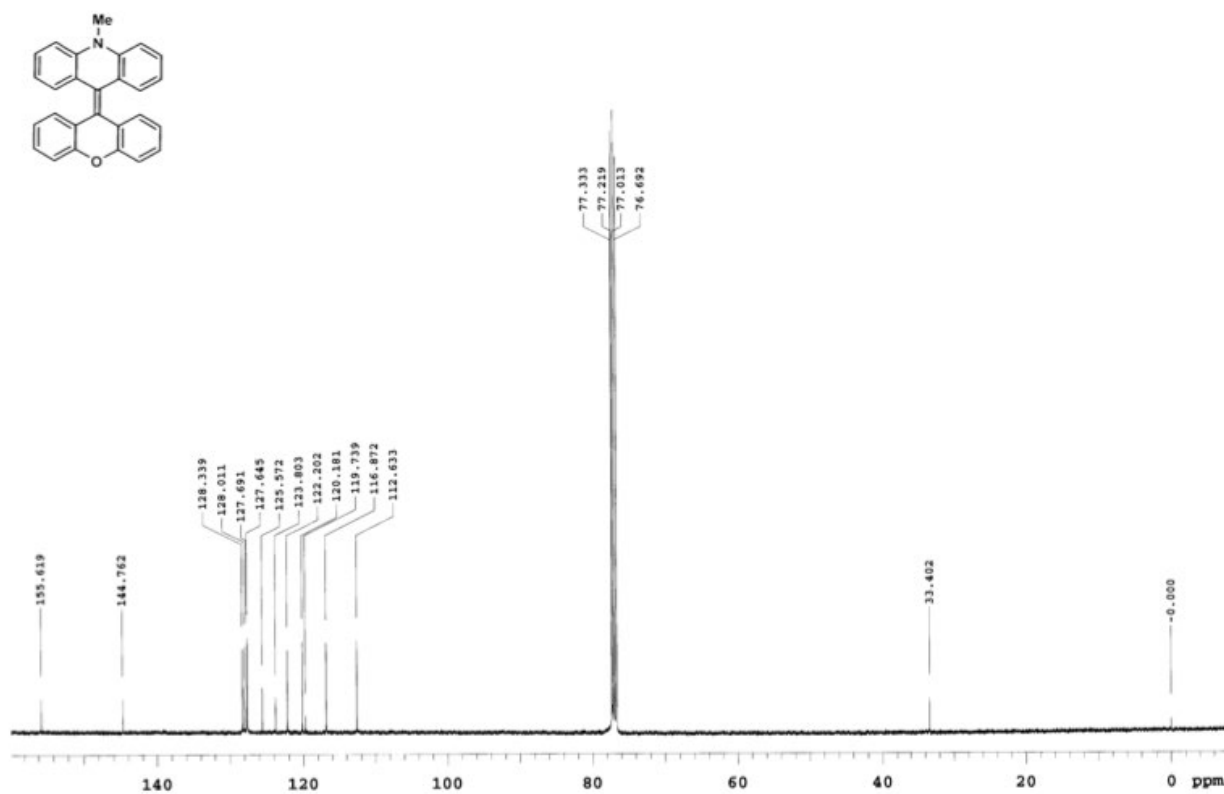


Figure S2.  $^{13}\text{C}$  NMR of 2a.

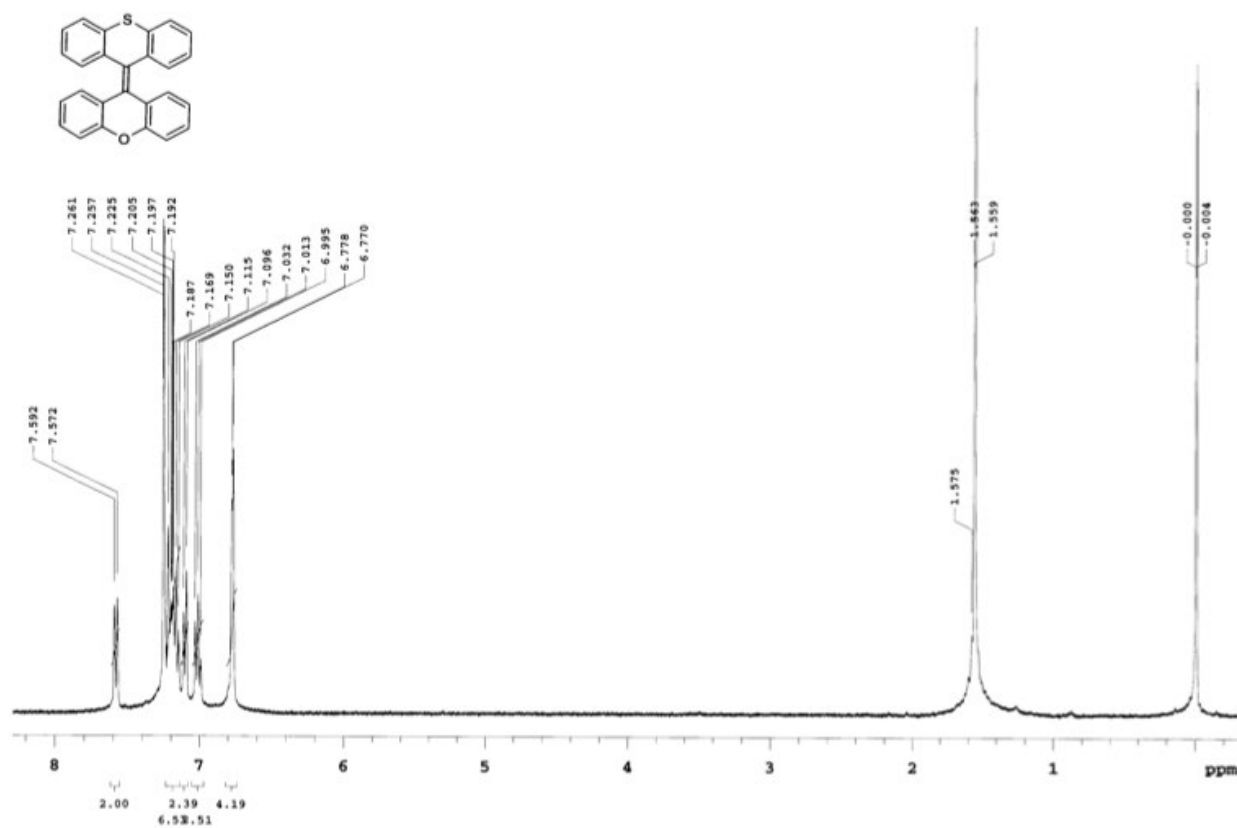


Figure S3. <sup>1</sup>H NMR of 3a.

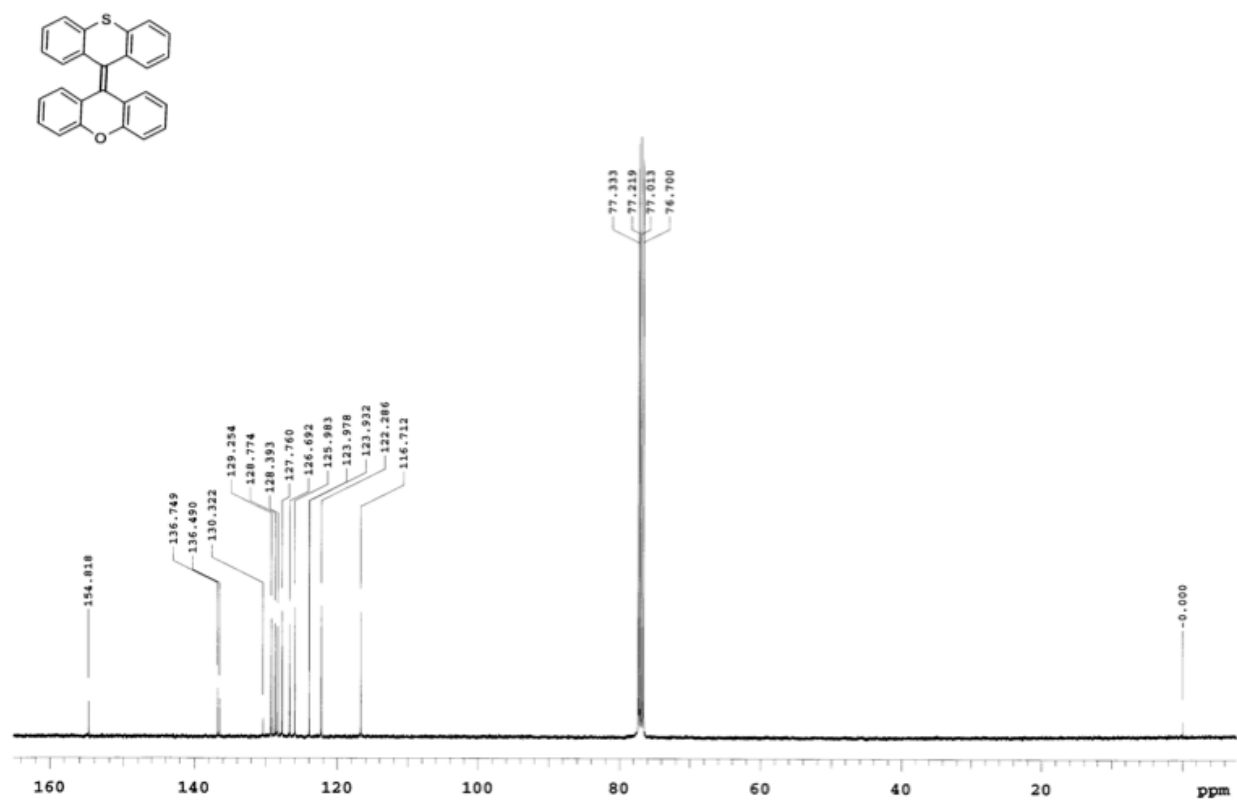


Figure S4. <sup>13</sup>C NMR of 3a.

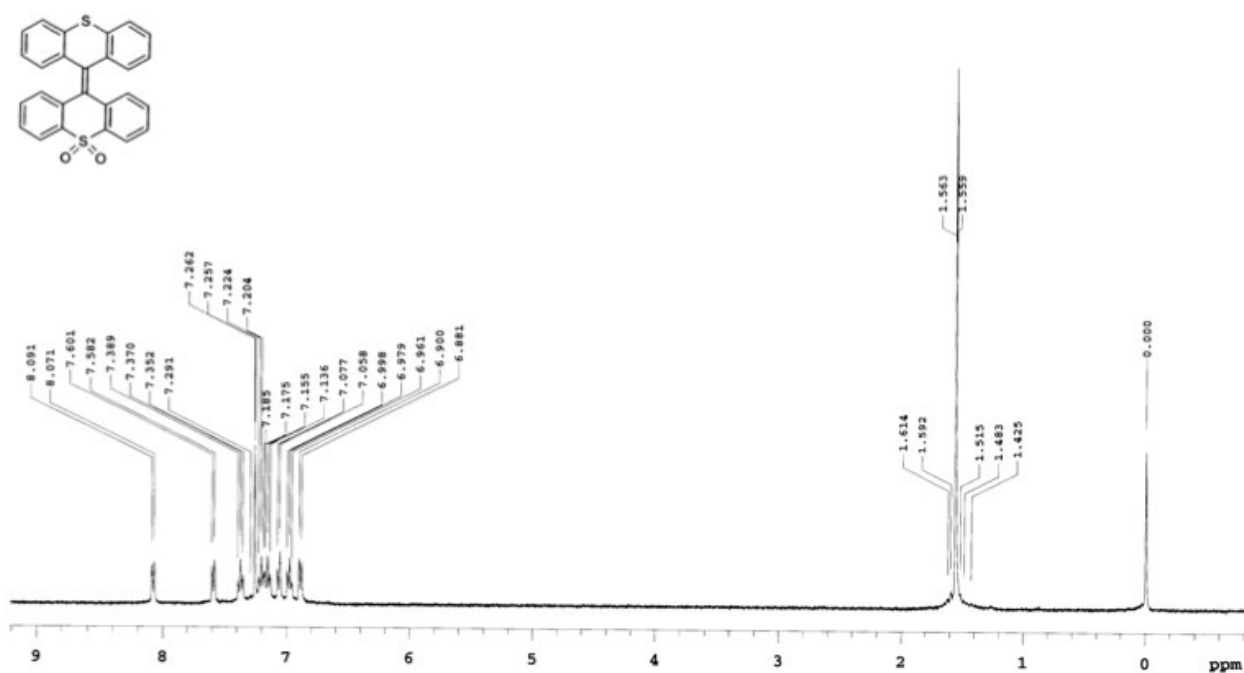


Figure S5. <sup>1</sup>H NMR of 3c.

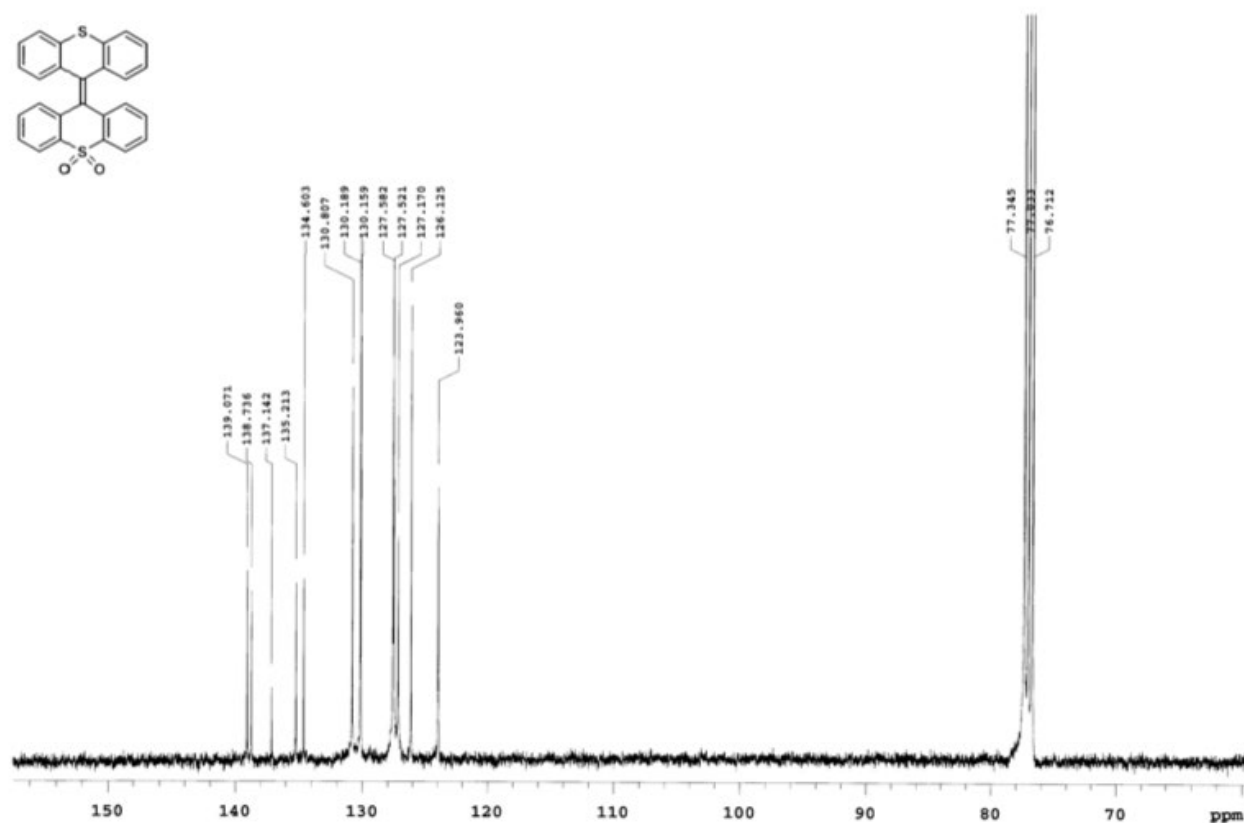


Figure S6. <sup>13</sup>C NMR of 3c.

## Fluorescence data including radiative rate constants and nonradiative rate constants of 1, 2, and 3

**Table S1.** Fluorescence data of **1**, **2**, and **3**.

1–3	In toluene <sup>[a]</sup>					In the solid state <sup>[b]</sup>					In PMMA <sup>[c]</sup>				
	$\lambda_{\text{em}}$ <sup>[d]</sup>	$\Phi$ <sup>[e]</sup>	$\tau$ <sup>[f]</sup>	$k_{\text{r}}$ <sup>[g]</sup>	$k_{\text{nr}}$ <sup>[h]</sup>	$\lambda_{\text{em}}$ <sup>[d]</sup>	$\Phi$ <sup>[e]</sup>	$\tau$ <sup>[f]</sup>	$k_{\text{r}}$ <sup>[g]</sup>	$k_{\text{nr}}$ <sup>[h]</sup>	$\lambda_{\text{em}}$ <sup>[d]</sup>	$\Phi$ <sup>[e]</sup>	$\tau$ <sup>[f]</sup>	$k_{\text{r}}$ <sup>[g]</sup>	$k_{\text{nr}}$ <sup>[h]</sup>
<b>1a</b>	475	0.20	1.3	1.54	6.15	520	0.81	5.92	1.37	0.32	478	0.81	5.49	1.48	0.35
<b>1b</b>	476	0.32	1.9	1.68	3.58	494	0.67	4.42	1.52	0.75	476	0.91	5.56	1.64	0.16
<b>1c</b>	493	0.04	0.3	1.33	32.0	513	0.76	4.95	1.54	0.48	496	0.82	4.87	1.68	0.37
<b>2a</b>	478	0.37	2.4	1.54	2.63	519	0.45	6.22	0.72	0.88	484	0.84	6.52	1.29	0.25
<b>2b</b>	478	0.48	3.2	1.50	1.63	568	0.30	6.49	0.46	1.08	478	0.91	5.98	1.52	0.15
<b>2c</b>	494	0.06	0.4	1.50	23.5	521	0.67	5.34	1.25	0.62	506	0.80	5.95	1.34	0.34
<b>3a</b>	435	0.32	1.8	1.78	3.78	443	0.88	4.66	1.89	0.26	429	0.67	4.02	1.67	0.82
<b>3c</b>	441	0.40	2.2	1.82	2.73	448	0.60	3.54	1.69	1.13	437	0.59	4.13	1.43	0.99

[a] Excitation wavelengths [nm]: 405 for **1a** and **2a**, 396 for **1b** and **2b**, 420 for **1c** and **2c**, 355 for **3a**, and 325 for **3c**. [b] Powder: **1a**, **1b**, **2b**, **2c**; microcrystalline solid: **1c**, **2a**, **3a**, **3c**. Excitation wavelength [nm]: 405 for **1a**, 396 for **1b**, 420 for **1c**, 405 for **2a**, 396 for **2b**, 420 for **2c**, 355 for **3a**, and 325 for **3c**. [c] Excitation wavelength [nm]: 405 for **1a**, 396 for **1b**, 380 for **1c**, 405 for **2a**, 396 for **2b**, 420 for **2c**, 355 for **3a**, and 325 for **3c**. [d]  $\lambda_{\text{em}}$ : Fluorescence maximum [nm]. [e]  $\Phi$ : Fluorescence quantum yield. [f]  $\tau$ : Fluorescence lifetime [ns]. [g]  $k_{\text{r}}$ : Radiative rate constant [ $10^8 \text{ s}^{-1}$ ]. [h]  $k_{\text{nr}}$ : Nonradiative rate constant [ $10^8 \text{ s}^{-1}$ ].

## Fluorescence data and spectra of **1b** and **2c** in polymer film

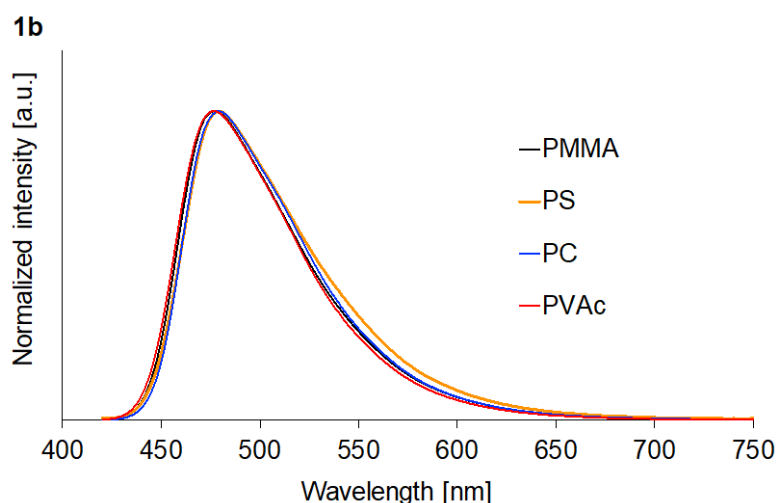
**Film Preparation:** Poly(methyl methacrylate) (PMMA) was purchased from Wako. Polystyrene (PS), poly(bisphenol A carbonate) (PC), and poly(vinyl acetate) (PVAc) were purchased from Sigma-Aldrich. Each polymer (200 mg) and **1b** or **2c** (0.2 mg) were dissolved in 2 mL of toluene (for **1b**) or CHCl<sub>3</sub> (for **2c**), respectively, at 60 °C. The solutions were spin-coated on a quartz plate at 1500 rpm to prepare thin films, which were dried under vacuum before measurement.

As shown in Table S2, the highest fluorescence quantum yields were observed when the BAEs were dispersed in PMMA. The fluorescence spectra were almost the same regardless of the host polymers.

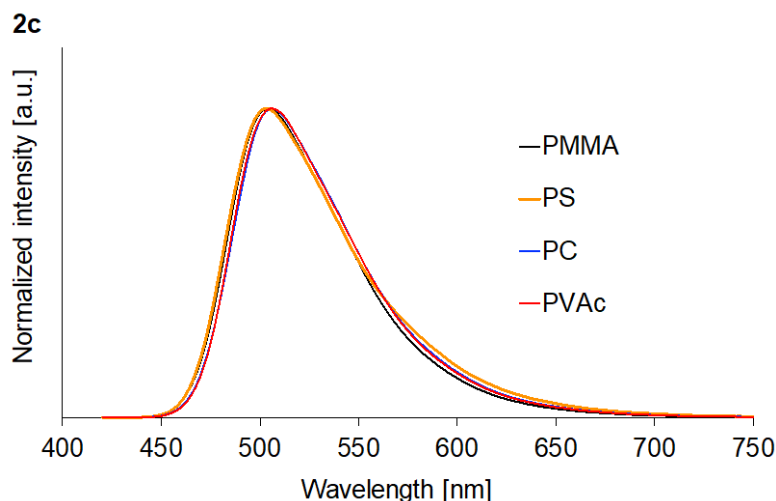
**Table S2.** Fluorescence data of **1b** and **2c** in polymer films.

	Fluorescence maxima in polymer film <sup>a</sup> (fluorescence quantum yield)			
Host polymer	PMMA	PS	PC	PVAc
<b>1b</b>	478 (0.91)	478 (0.87)	479 (0.83) <sup>b</sup>	476 (0.89)
<b>2c</b>	504 (0.80)	503 (0.73)	505 (0.71)	506 (0.74)

<sup>a</sup> Absolute quantum yields were recorded using a calibrated integrating sphere. <sup>b</sup> The doped film was prepared from a THF solution of **1b** and PC due to the low solubility of PC in toluene.

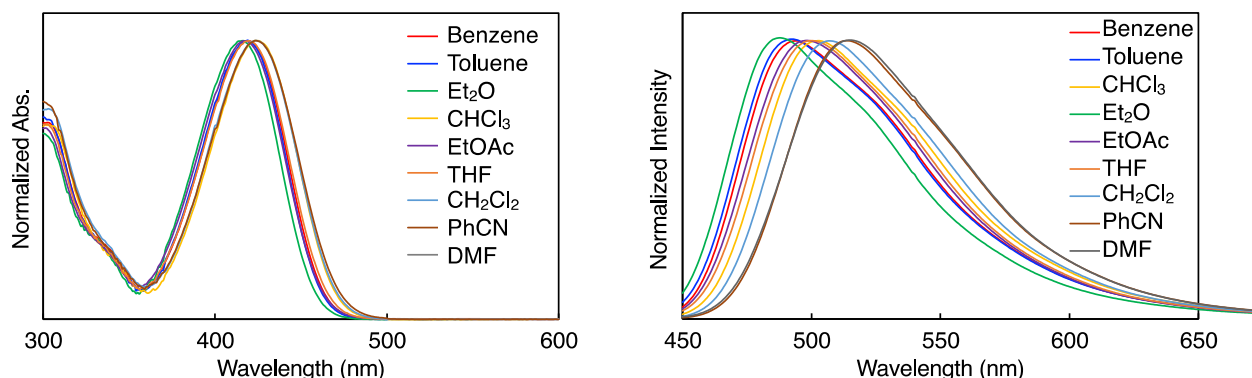


**Figure S7.** Fluorescence spectra of **1b** in polymer film.



**Figure S8.** Fluorescence spectra of **2c** in polymer film.

## Lippert–Mataga Study on 1c and 2c

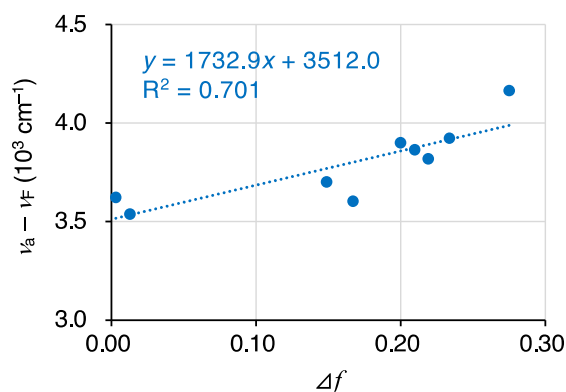


**Figure S9.** Absorption and fluorescence spectra of **1c** in various solvents. Excitation wavelength in fluorescence spectra is 420 nm.

**Table S3.** Orientational polarizability ( $\Delta f$ ), wavelength of absorption maximum ( $\lambda_{\text{abs}}$ ), wavelength of fluorescence maximum ( $\lambda_{\text{F}}$ ), wave number of absorption maximum ( $\nu_{\text{a}}$ ), wave number of fluorescence maximum ( $\nu_{\text{F}}$ ), and Stokes shift ( $\nu_{\text{a}} - \nu_{\text{F}}$ ) of **1c**.

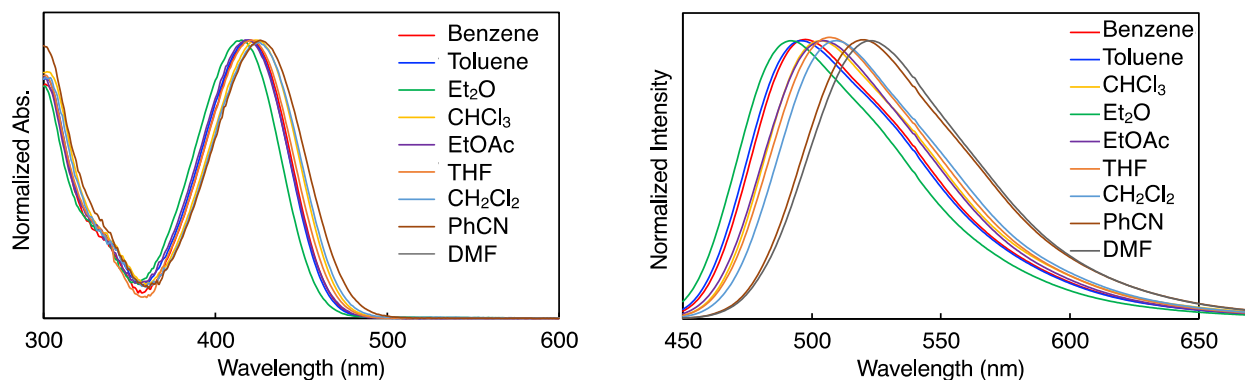
solvent	$\Delta f^a$	$\lambda_{\text{abs}}$ (nm)	$\lambda_{\text{F}}$ (nm)	$\nu_{\text{a}}$ ( $\text{cm}^{-1}$ )	$\nu_{\text{F}}$ ( $\text{cm}^{-1}$ )	$\nu_{\text{a}} - \nu_{\text{F}}$ ( $\text{cm}^{-1}$ )
benzene	0.003	419.0	494.0	$2.39 \times 10^4$	$2.02 \times 10^4$	$3.62 \times 10^3$
toluene	0.013	419.0	492.0	$2.39 \times 10^4$	$2.03 \times 10^4$	$3.54 \times 10^3$
$\text{CHCl}_3$	0.149	424.0	503.0	$2.36 \times 10^4$	$1.99 \times 10^4$	$3.70 \times 10^3$
$\text{Et}_2\text{O}$	0.167	415.0	488.0	$2.41 \times 10^4$	$2.05 \times 10^4$	$3.60 \times 10^3$
EtOAc	0.200	417.0	498.0	$2.40 \times 10^4$	$2.01 \times 10^4$	$3.90 \times 10^3$
THF	0.210	419.0	500.0	$2.39 \times 10^4$	$2.00 \times 10^4$	$3.87 \times 10^3$
$\text{CH}_2\text{Cl}_2$	0.219	424.0	506.0	$2.36 \times 10^4$	$1.98 \times 10^4$	$3.82 \times 10^3$
PhCN	0.234	427.0	427.0	$2.34 \times 10^4$	$1.95 \times 10^4$	$3.93 \times 10^3$
DMF	0.275	424.0	515.0	$2.36 \times 10^4$	$1.94 \times 10^4$	$4.17 \times 10^3$

a) The values of orientational polarizability ( $\Delta f$ ) are cited from Table 7.2 in page 211 of a book “Molecular Fluorescence, B. Valeur, Wiley–VCH, Weinheim, 2002” and Table S3 in B. Yang, et al. *Adv. Funct. Mater.* **2019**, 29, 1901895.



**Figure S10.** Lippert–Mataga plots of **1c**.



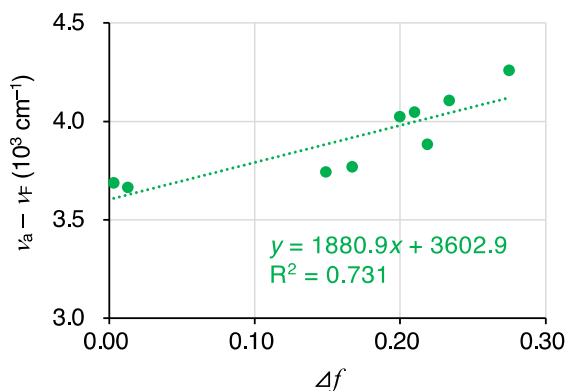


**Figure S11.** Absorption and fluorescence spectra of **2c** in various solvents. Excitation wavelength in fluorescence spectra is 420 nm.

**Table S4.** Orientational polarizability ( $\Delta f$ ), wavelength of absorption maximum ( $\lambda_{\text{abs}}$ ), wavelength of fluorescence maximum ( $\lambda_{\text{F}}$ ), wave number of absorption maximum ( $\nu_{\text{a}}$ ), wave number of fluorescence maximum ( $\nu_{\text{F}}$ ), and Stokes shift ( $\nu_{\text{a}} - \nu_{\text{F}}$ ) of **2c**.

solvent	$\Delta f^a$	$\lambda_{\text{abs}}$ (nm)	$\lambda_{\text{F}}$ (nm)	$\nu_{\text{a}}$ ( $\text{cm}^{-1}$ )	$\nu_{\text{F}}$ ( $\text{cm}^{-1}$ )	$\nu_{\text{a}} - \nu_{\text{F}}$ ( $\text{cm}^{-1}$ )
benzene	0.003	420.0	497.0	$2.38 \times 10^4$	$2.01 \times 10^4$	$3.69 \times 10^3$
toluene	0.013	419.0	495.0	$2.39 \times 10^4$	$2.02 \times 10^4$	$3.66 \times 10^3$
$\text{CHCl}_3$	0.149	424.0	504.0	$2.36 \times 10^4$	$1.98 \times 10^4$	$3.74 \times 10^3$
$\text{Et}_2\text{O}$	0.167	415.0	492.0	$2.41 \times 10^4$	$2.03 \times 10^4$	$3.77 \times 10^3$
EtOAc	0.200	419.0	504.0	$2.39 \times 10^4$	$1.98 \times 10^4$	$4.03 \times 10^3$
THF	0.210	420.0	506.0	$2.38 \times 10^4$	$1.98 \times 10^4$	$4.05 \times 10^3$
$\text{CH}_2\text{Cl}_2$	0.219	425.0	509.0	$2.35 \times 10^4$	$1.96 \times 10^4$	$3.88 \times 10^3$
PhCN	0.234	428.5	520.0	$2.33 \times 10^4$	$1.92 \times 10^4$	$4.11 \times 10^3$
DMF	0.275	427.0	522.0	$2.34 \times 10^4$	$1.92 \times 10^4$	$4.26 \times 10^3$

a) The values of orientational polarizability ( $\Delta f$ ) are cited from Table 7.2 in page 211 of a book “Molecular Fluorescence, B. Valeur, Wiley–VCH, Weinheim, 2002” and Table S3 in B. Yang, et al. *Adv. Funct. Mater.* **2019**, 29, 1901895.



**Figure S12.** Lippert–Mataga plots of **2c**.