

Supporting Information

Organic Dopant Cyclization and Significantly Improved RTP Properties

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Experimental Procedure

^1H spectra were recorded on AC500 spectrometer (Bruker, Germany) at 500 MHz, respectively. The steady-state photoluminescence spectra were recorded on Hitachi F-4600 spectrophotometer. The ultraviolet absorption spectra were tested using a Hitachi model U-4100 ultraviolet spectrophotometer. Absolute PL quantum yields (PL efficiency) were determined with an integrating sphere spectrometer C11347 (Hamamatsu, Japan). Time-resolved spectra were recorded by an Edinburgh Instruments modular fluorescence lifetime spectrometer (FLS-1000). The lifetimes (τ) of the luminescence were obtained by fitting the decay curve with a multi-exponential decay function of

$$R(t) = \sum_i B_i e^{-\frac{t}{\tau_i}} \quad (\text{S1})$$

where B_i and τ_i represent the amplitudes and lifetimes of the individual components for multi-exponential decay profiles, respectively. The digital photographs were captured by the FDR-AX700 4K HDR digital cameras (SONY, Japan). The low temperature photoluminescence spectra were performed on a QE Pro spectrometer with a CCD array (Ocean Optics) as a power detector.

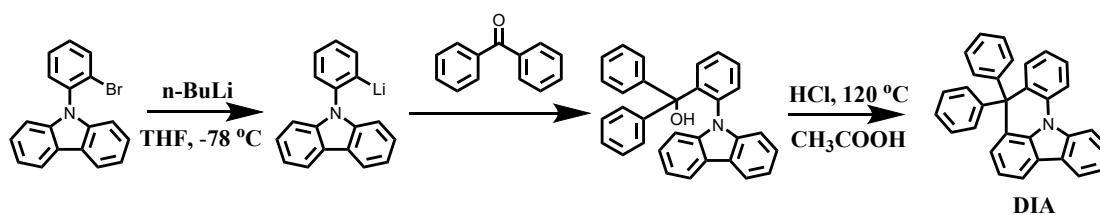
The Gaussian 09 program was utilized to perform the TD-DFT calculations. The exciton energies of the n -th singlet (S_n) and n -th triplet states (T_n) were obtained on the corresponding ground state structure using TD-B3LYP/6-31G*. The Kohn–Sham frontier orbital analysis and spin density distributions were obtained to elucidate the mechanisms of possible singlet–triplet intersystem crossings (ISC).

Materials

Polymethyl methacrylate (PMMA, CM-211, molecular weight: 80000-200000) and acrylonitrile butadiene styrene (ABS, PA-709) were obtained from Chi Mei Co., Ltd (Taiwan, China). All other chemicals and solvents were purchased from Energy Chemical Co., Ltd (Shanghai, China) and used with further purification.

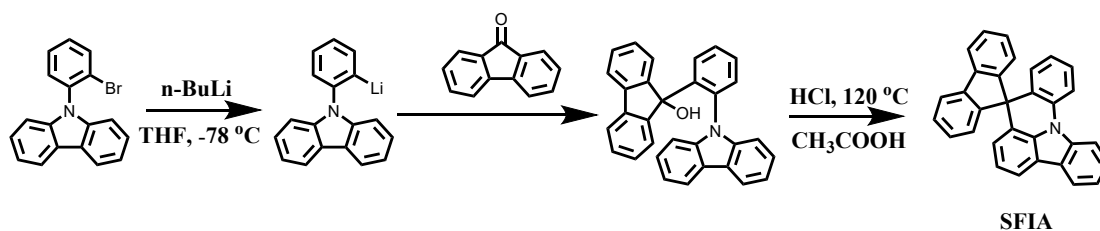
Dopant molecular synthesis

8,8-diphenyl-8H-indolo[3,2,1-de]acridine (DIA)



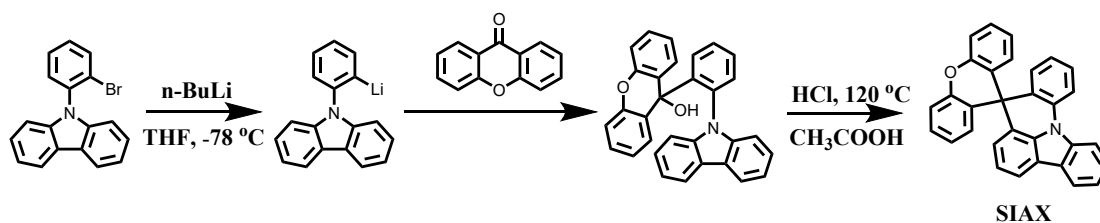
In a 100 mL bottom flask, 9-(2-Bromophenyl)-9H-carbazole (2.1 g, 6.6 mmol) were dissolved in tetrahydrofuran (THF) (20 mL) in a nitrogen environment. Cool the mixture to -78 °C and slowly add *n*-BuLi (3.4 mL). The mixture was stirred at -78 °C for 2 h. Dissolving benzophenone (1.5 g, 8.5 mmol) in THF (10 mL) under nitrogen conditions. The mixture was stirred for another 30 minutes at -78 °C and allowed warming up to room temperature gradually and then add saturated NaHCO₃. The mixture was poured into water and extracted with dichloromethane, the combined organic layer was dried with anhydrous MgSO₄, filtered and concentrated in vacuo. The crude product was purified by silica gel column chromatography using petroleum ether/dichloromethane (2:1, v/v) as the eluent, yielding a white solid (2.02 g, yield 56%). Dissolve the obtained powder in acetic acid (20ml) and add a catalytic amount of HCl) aqueous solution (5 mol% 12N). Reflux at 120 °C for 12 h. The mixture was poured into water and extracted with dichloromethane, the combined organic layer was dried with anhydrous MgSO₄, filtered and concentrated in vacuo. The crude product was purified by silica gel column chromatography using petroleum ether/dichloromethane (3:1, v/v) as the eluent, yielding a white solid (1.12 g, yield 52%).¹H NMR (500 MHz, DMSO-*d*₆) δ 8.32 – 8.27 (m, 2H), 8.23 (dd, *J* = 8.3, 1.2 Hz, 1H), 8.11 (dd, *J* = 7.7, 1.0 Hz, 1H), 7.60 (ddd, *J* = 8.4, 7.2, 1.3 Hz, 1H), 7.47 (ddd, *J* = 8.4, 7.3, 1.6 Hz, 1H), 7.40 (td, *J* = 7.7, 1.4 Hz, 2H), 7.33 – 7.27 (m, 4H), 7.27 – 7.22 (m, 2H), 7.18 (td, *J* = 7.6, 1.1 Hz, 1H), 7.01 – 6.95 (m, 6H). ¹³C NMR (126 MHz, DMSO) δ 146.29, 138.23, 136.98, 136.50, 131.94, 130.06, 128.62, 128.48, 127.97, 127.44, 127.18, 126.40, 126.35, 123.64, 123.10, 122.11, 121.93, 119.06, 115.05, 114.12, 56.94, 40.58, 40.49, 40.42, 40.32, 40.25, 40.16, 40.08, 39.99, 39.83, 39.66, 39.49.

Spiro[fluorene-9,8'-indolo[3,2,1-de]acridine] (CDIA)



The synthesis steps are the same as DIA, only replacing benzophenone with 9 fluorenone. The crude product was purified by silica gel column chromatography using petroleum ether/dichloromethane (3:1, v/v), yielding a white solid (2.24 g, yield 58%). ¹H NMR (500 MHz, Chloroform-*d*) δ 8.30 (d, *J* = 8.3 Hz, 1H), 8.24 (d, *J* = 8.3 Hz, 1H), 8.20 (d, *J* = 7.7 Hz, 1H), 7.86 (dd, *J* = 18.3, 7.6 Hz, 3H), 7.64 (ddd, *J* = 8.5, 7.2, 1.4 Hz, 1H), 7.45 – 7.30 (m, 4H), 7.21 – 7.11 (m, 4H), 7.08 (t, *J* = 7.6 Hz, 1H), 6.85 (t, *J* = 7.5 Hz, 1H), 6.63 (dd, *J* = 7.8, 1.6 Hz, 1H), 6.53 (d, *J* = 7.5 Hz, 1H), 5.36 – 5.24 (m, 12H). ¹³C NMR (126 MHz, DMSO) δ 155.41, 139.46, 136.77, 136.35, 129.07, 129.04, 129.01, 128.89, 128.54, 127.64, 125.94, 125.62, 124.54, 123.98, 123.15, 123.09, 122.61, 121.86, 121.76, 121.01, 118.91, 115.24, 114.49, 56.70, 40.50, 40.42, 40.33, 40.25, 40.16, 40.00, 39.92, 39.83, 39.66, 39.50. MS: *m/z* Calcd for C₃₁H₁₉N: 405.1517; found 405.1513 [M]⁺.

Spiro[indolo[3,2,1-de]acridine-8,9'-xanthene] (ODIA)



The synthesis steps are the same as DIA, only replacing benzophenone with xanthone. The crude product was purified by silica gel column chromatography using petroleum ether/dichloromethane (3:1, v/v), yielding a white solid (1.85 g, yield 53%). ¹H NMR (500 MHz, DMSO-*d*₆) δ 8.47 (d, *J* = 8.5 Hz, 1H), 8.34 (ddd, *J* = 12.6, 8.1, 1.2 Hz, 2H), 8.02 (dd, *J* = 7.7, 1.0 Hz, 1H), 7.68 – 7.64 (m, 1H), 7.45 – 7.38 (m, 2H), 7.28 – 7.19 (m, 5H), 7.06 – 7.02 (m, 1H), 6.97 (dd, *J* = 7.9, 1.7 Hz, 1H), 6.89 (ddd, *J* = 8.2, 6.9, 1.5 Hz, 2H), 6.80 (dd, *J* = 7.5, 1.0 Hz, 1H), 6.75 (dd, *J* = 7.9, 1.5 Hz, 2H). ¹³C NMR (126 MHz, DMSO) δ 148.44, 138.19, 135.17, 133.93, 133.58, 131.67, 130.19, 128.79, 128.72, 127.82, 126.66, 125.78, 124.44, 124.30, 123.54, 122.07, 121.92, 121.75,

118.70, 116.57, 114.76, 114.24, 44.88, 40.60, 40.50, 40.43, 40.34, 40.26, 40.17, 40.09, 40.00, 39.93, 39.84, 39.67, 39.50. MS: m/z Calcd for $C_{31}H_{19}NO$: 421.1467; found 421.1459 $[M]^+$.

Preparation of organic doped polymers

DIA, CDIA and ODIA were dissolved into PMMA/ABS solution in dichloromethane by 0.1% weight ratio vs polymer and evaporated into film. The film is taken out and further dried in oven at 80-100 °C for 12 h. Then, film was thermoplasticized on an open two-roll mill ca. 2 min at 145 °C for PMMA/ABS. The thermoplasticized film was molded into 3 cm × 3 cm × 1 mm plate on a flat vulcanizer under 5 MPa for 3 min at 190 °C for PMMA/ABS. After cooling under 2 MPa at room temperature. A smoothing sheet was obtained after cold pressing.

Figures and Tables

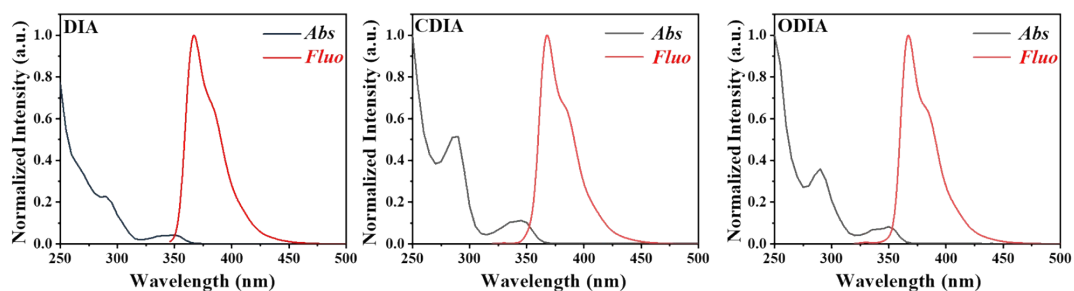


Figure S1. The ultraviolet-visible absorption spectra (Abs.), fluorescent spectra (Fluo.) in dilute tetrahydrofuran (THF) solution.

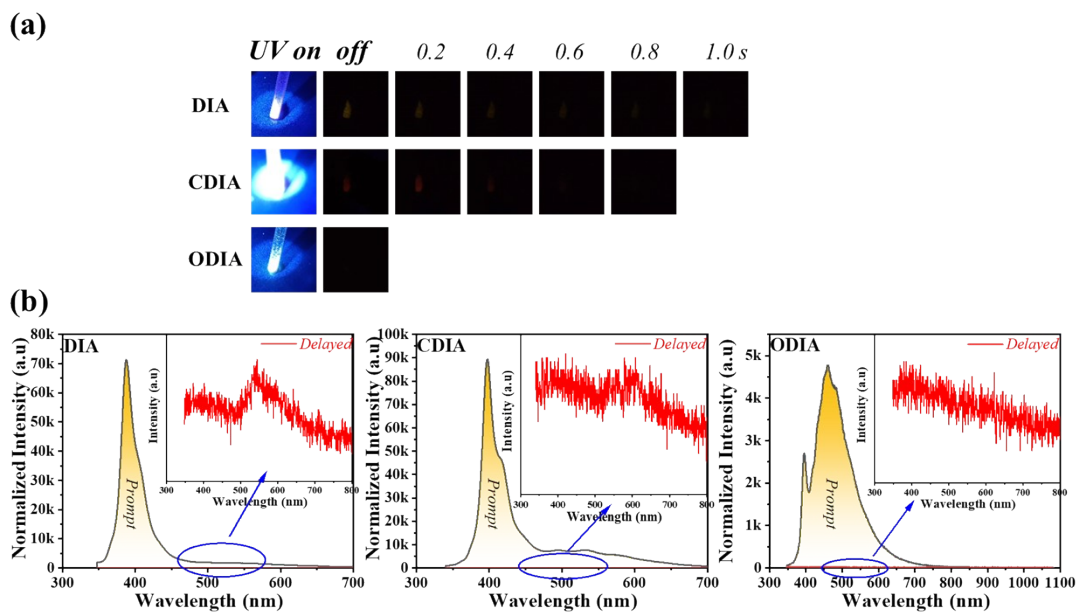


Figure S2. (a) The room temperature PL photographs of DIA, SFIA and SIAX powder. (b) The room temperature prompt and delayed PL spectra of DIA, CDIA and ODIA powder under 310 nm light excitation.

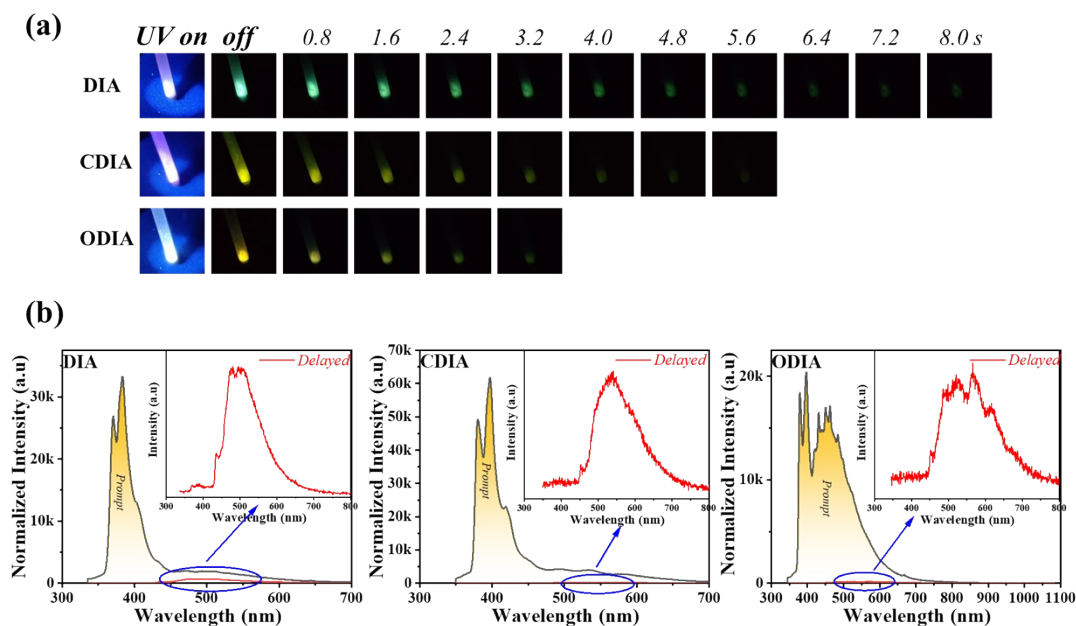


Figure S3. (a) The low temperature PL photographs of DIA, SFIA and SIAX powder. (b) The low temperature prompt and delayed PL spectra of DIA, CDIA and ODIA powder under 310 nm light excitation.

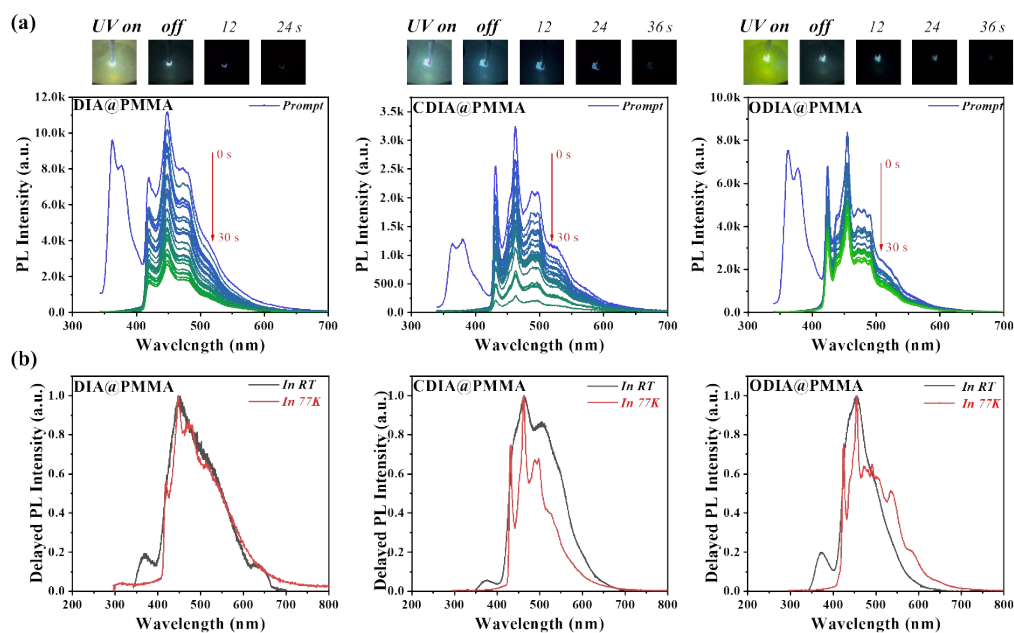


Figure S4. (a) Low temperature photos and prompt spectra of DIA@PMMA, SFIA@PMMA and SIAX@PMMA, as well as delayed decay spectra from 0 to 30 s. (b) Comparison of delayed spectra of DIA@PMMA, CDIA@PMMA and ODIA@PMMA under room temperature and low temperature conditions.

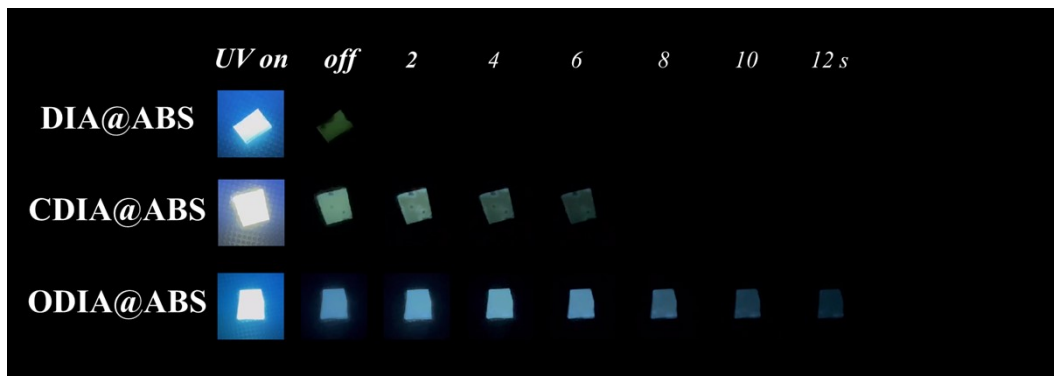


Figure S5. The room temperature PL photographs of DIA, CDIA and ODIA (0.1%) in ABS after removing 365 nm UV light (3 mW/cm^2).

pdata/1
PROTON DMSO [E:\data\test2023] test 15

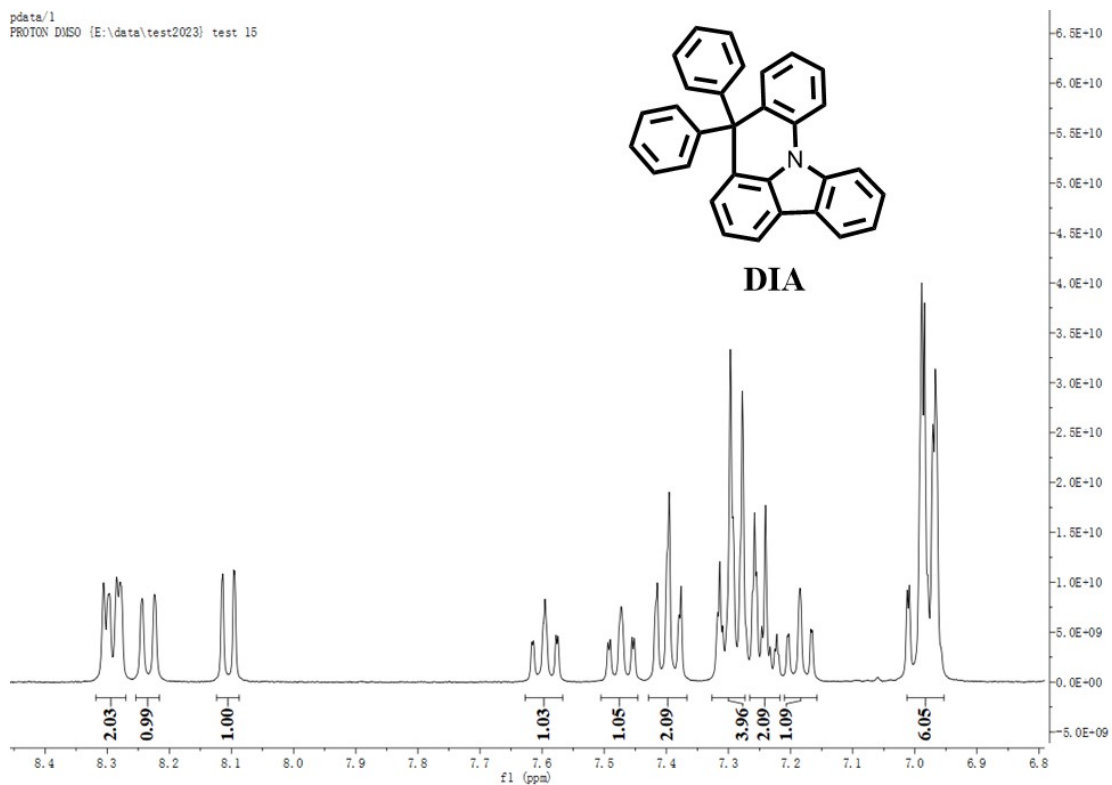


Figure S6. ^1H spectrum of DIA in $\text{DMSO-}d_6$.

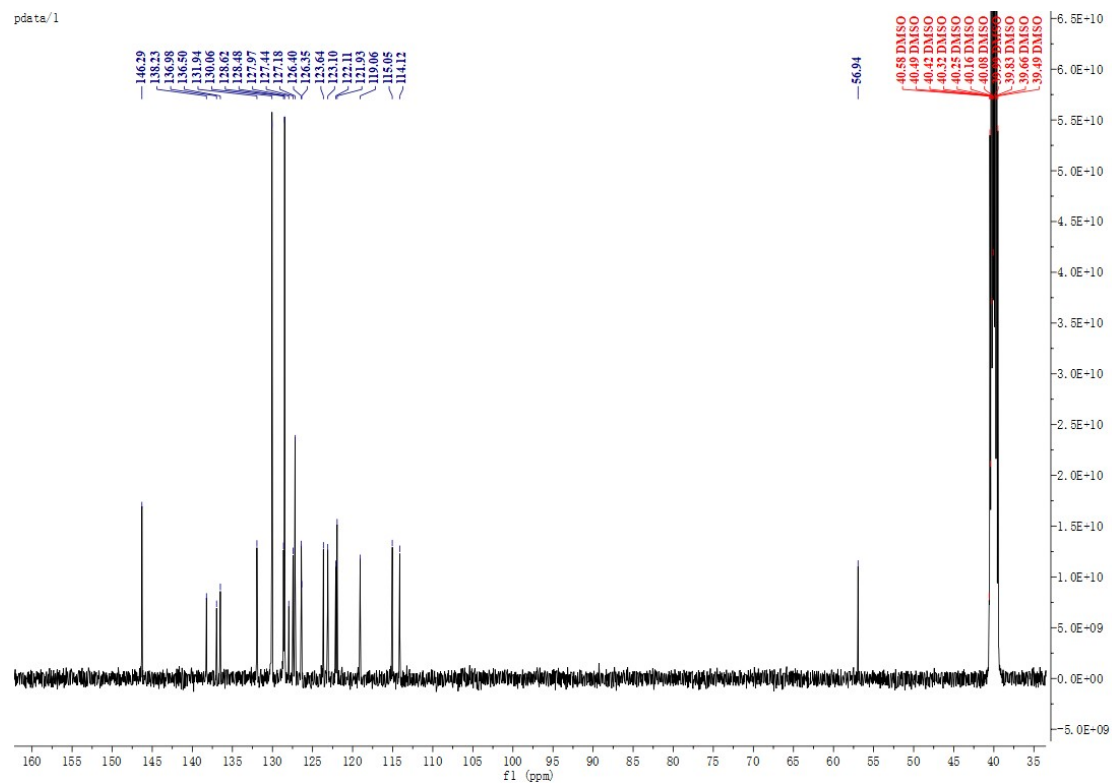


Figure S7. ^{13}C spectrum of DIA in $\text{DMSO-}d_6$.

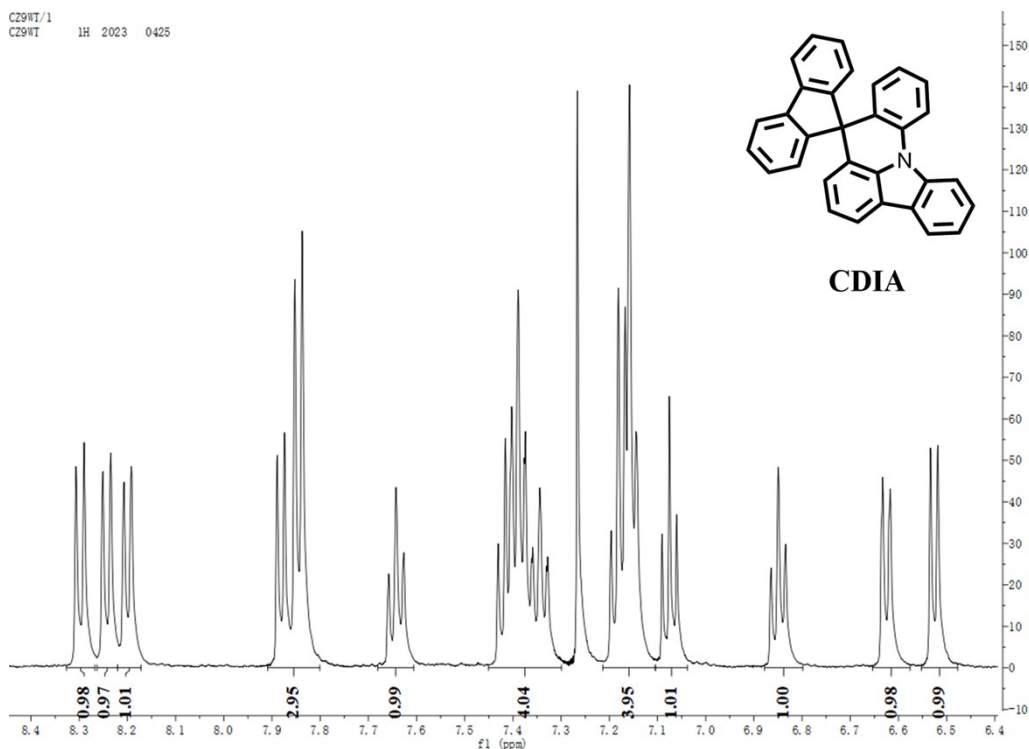


Figure S8. ^1H spectrum of CDIA in Chloroform- d .

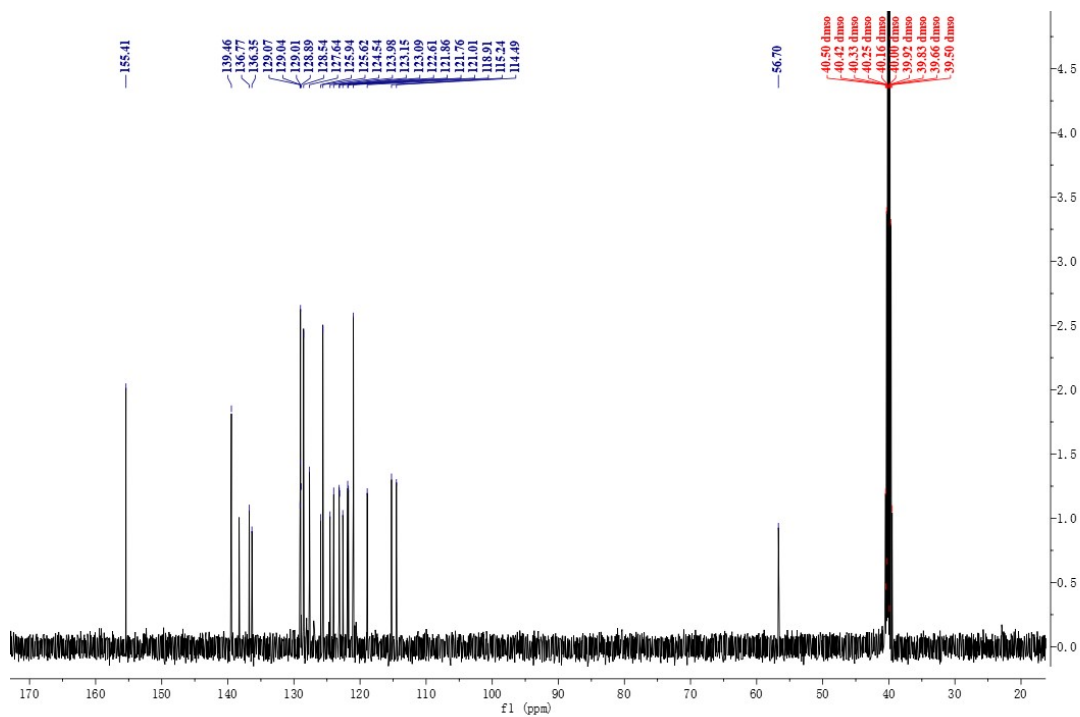


Figure S9. ^{13}C spectrum of CDIA in DMSO- d_6 .

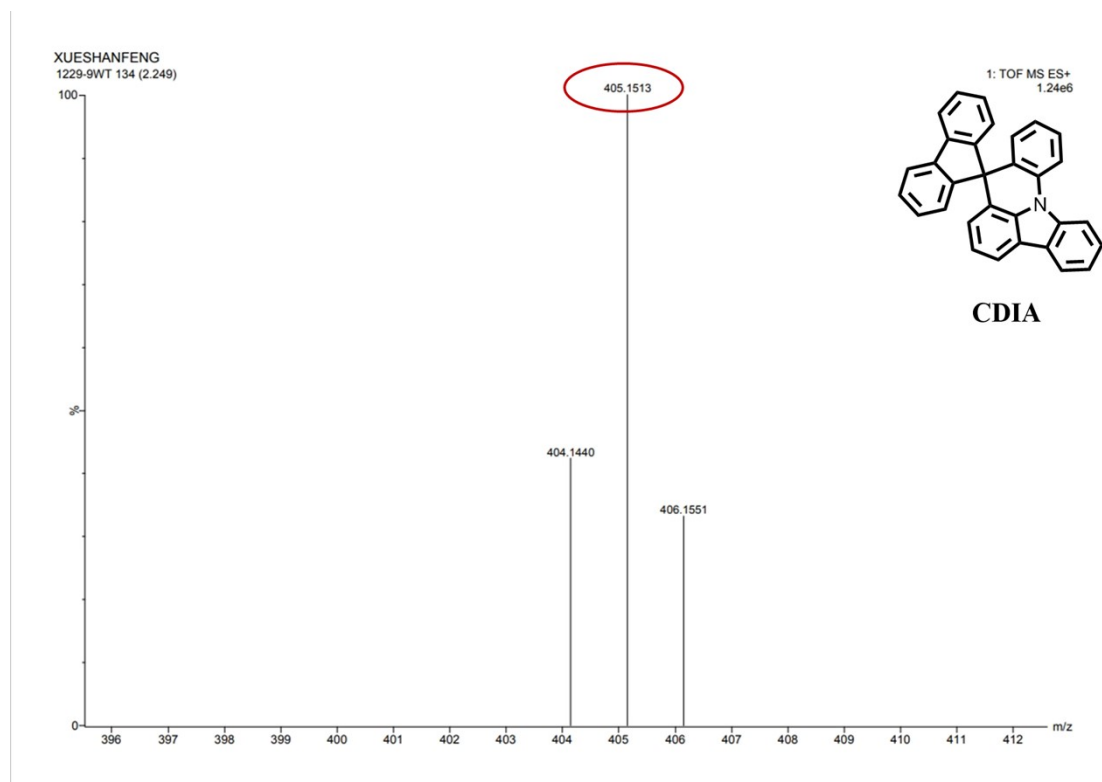


Figure S10. HR Mass Spectrum (M^+) of CDIA.

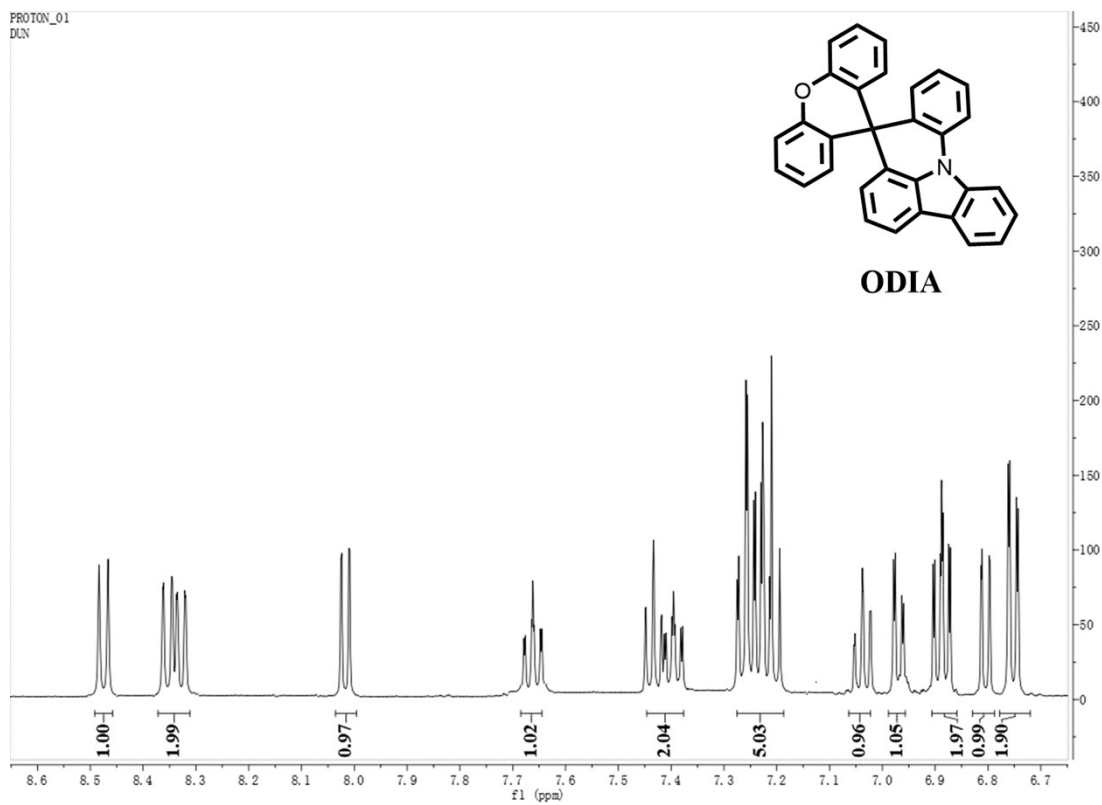


Figure S11. ^1H spectrum of ODIA in $\text{DMSO-}d_6$.

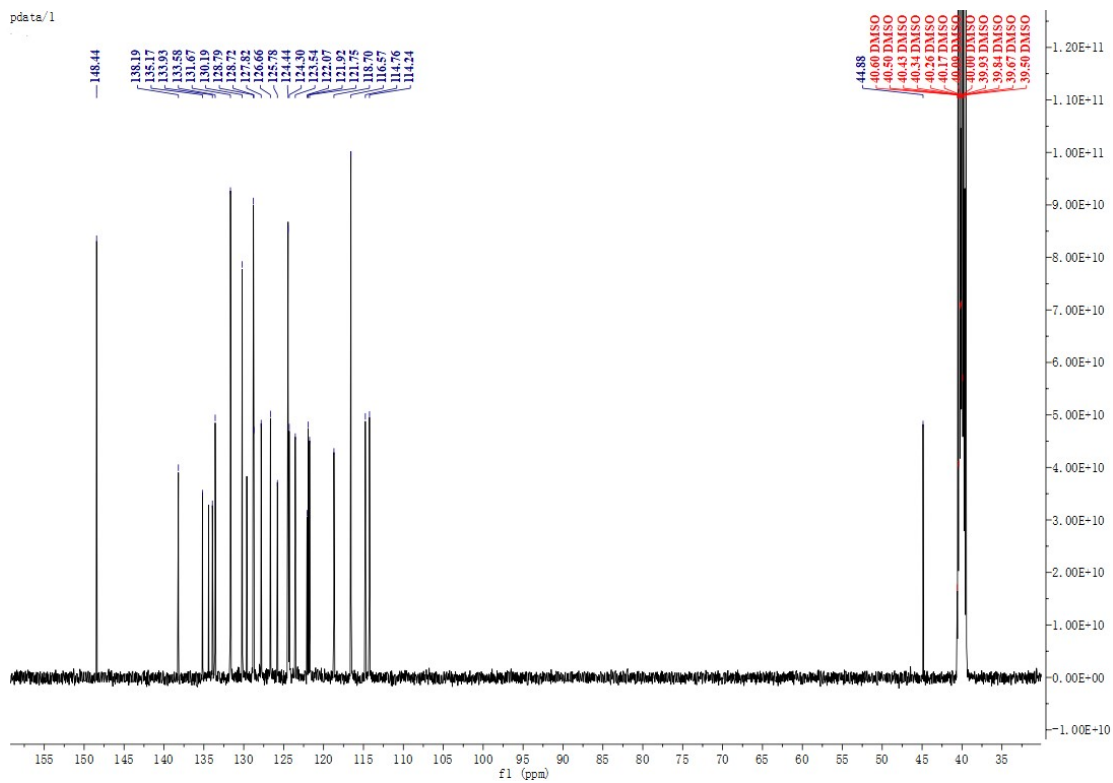


Figure S12. ^{13}C spectrum of ODIA in $\text{DMSO-}d_6$.

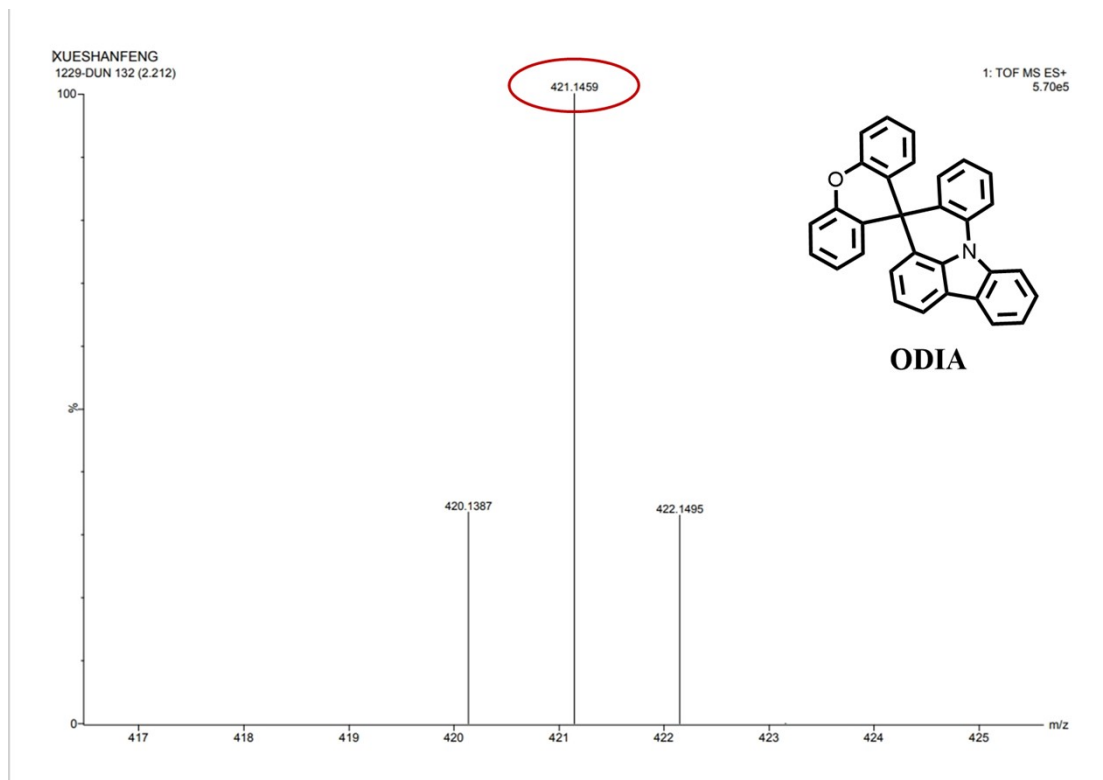


Figure S13. HR Mass Spectrum (M^+) of ODIA.

Table S1. Phosphorescence lifetimes of **DIA@PMMA**, **CDIA@PMMA** and **ODIA@PMMA** films.

Film	Component	τ_1	A_1	τ_2	A_2	τ_3	A_3	τ_P
		(ms)	(%)	(ms)	(%)	(ms)	(%)	(ms)
DIA@PMMA	449 nm	36.29	63.92	148.2	36.08	/	/	77
CDIA@PMMA	553 nm	75.49	4.59	568.9	26.96	2146	68.45	1619
ODIA@PMMA	454 nm	96.52	2.97	703.5	22.89	2656	74.14	2133

Table S2. Phosphorescence lifetimes of **CDIA/PR@PMMA** and **ODIA/PR@PMMA** films.

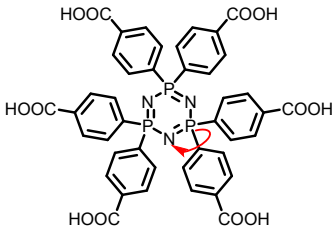
Film	Component	τ_1	A_1	τ_2	A_2	τ_3	A_3	τ_P
		(ms)	(%)	(ms)	(%)	(ms)	(%)	(ms)
CDIA/PR	629 nm	32.39	15.90	302.5	36.61	1567	47.49	860
ODIA/PR	629 nm	27.95	9.76	334.9	25.37	1800	64.87	1255

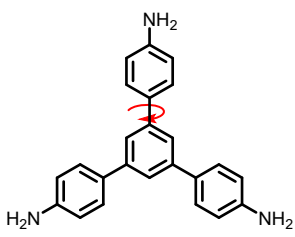
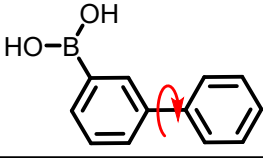
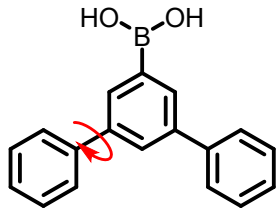
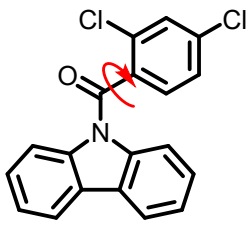
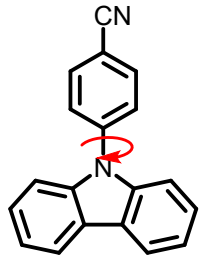
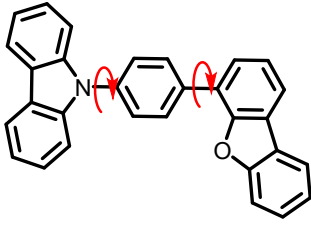
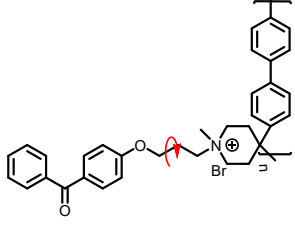
Table S3. Crystal data for **CDIA** and **ODIA**.

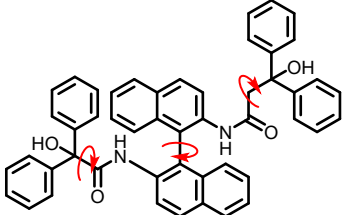
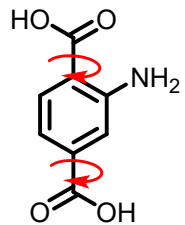
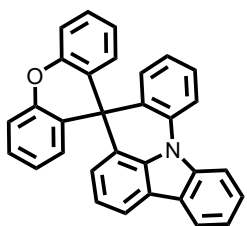
Compound	CDIA	ODIA
Chemical formula	$C_{124}H_{76}N_4$	$C_{31}H_{19}NO$
Formula weight	1621.88	421.47
Crystal system	triclinic	monoclinic
$a/\text{\AA}$	11.5151(5)	9.0420(2)
$b/\text{\AA}$	13.9307(6)	25.7448(7)
$c/\text{\AA}$	14.1697(6)	9.2981(2)

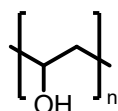
$\alpha/^\circ$	91.208(2)	90
$\beta/^\circ$	113.8220(10)	102.736(2)
$\gamma/^\circ$	93.799(2)	90
Unit cell volume/ \AA^3	2071.94(15)	2111.20(9)
Temperature/K	298(2)	299.0
Space group	P 1	P -2yc
Z	1	4
F(000)	848	880
Theta range for data collection	2.33 to 27.96	3.433 to 68.716
Index ranges	-13 \leq h \leq 13	-10 \leq h \leq 10
	-16 \leq k \leq 16	-26 \leq k \leq 31
	-16 \leq l \leq 16	-8 \leq l \leq 11
restraints / parameters	6/1153	4/595
CCDC number	2350554	2350558

Table S4. Typical organic room temperature phosphorescent materials with single bond rotation doped polymer.

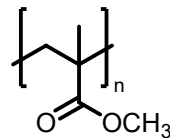
	Molecule	Polymer	τ_p	Cite
1		PVA	0.71 s	Sci. Adv., 2018, 4, eaas9732.

2		PVA	1.74 s	Mater. Horiz., 2022, 9, 1081.
3		PVA	2.43 s	Sci. Adv., 2022, 8, eabl8392.
4		PVA	2.43 s	Nat. Commun., 2022, 13, 347.
5		PMMA	0.03 s	Angew. Chem. Int. Ed., 2019, 131, 14278.
6		PMMA	0.52 s	Chem. Eng. J., 2022, 447, 137458.
7		PMMA	1.51 s	ACS Appl. Mater. Interfaces, 2021, 13, 41131.
8		PMMA	1.26 s	Adv. Mater. 2022, 34, 2204415.

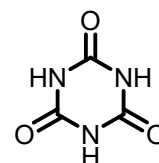
9		PAN	1.36 s	Chem. Sci. 2024, 15, 8052–8061.
10		CA	0.80 s	Adv.Funct. Mater.2024,34,23 10198.
11		PMMA	2.66 s	This work



PVA



PMMA



CA