Supporting information

A novel ionic AIE smart responsive material with multiple structural transformations

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Experimental Section

materials and method

Zn-dust, $TiCl_4$, diphenylmethanone, 4,4-dimethylbenzophenone were brought from Aldrich. N-Methylimidazole was obtained from Shanghai Weite Chemical Reagent Co., Ltd. N-bromosuccinimide was brought from Wuhan Pengo Technology., Ltd. AIBN was brought from Energy Chemical (China). All other chemicals were analytical grade reagents.

The ^1H NMR and ^{13}C NMR spectra of samples were obtained by using an INVOA 400 MHz spectrometer, High-resolution Mass spectrum (HRMS) was recorded using a Thermo Scientific Orbitrap Elite mass spectrometer. IR spectra (400–4000 cm^{-1}) were recorded on a Shimadzu IR Prestige-21 FT-IR. Spectrophotometer UV/Vis experiments were performed with a Shimadzu UV-2550 spectrometer, Fluorescence spectra were recorded by Edinburgh FLSP920. Temperature-dependent X-ray diffraction (XRD) were recorded by D8 ADVANCE

The HepG2 cells were grown in DMEM (Dulbecco's Modified Eagle's Medium) supplemented with 10% FBS (fetal bovine serum), 2 mM of glutamine, penicillin (100 units/mL), and streptomycin (100 units/mL) at 37 °C. They were treated with $[TPE\text{-}Dim\text{-}DMe]^{2+}[Br]_2^{2-}$ (0.5mM) in culture media for 30 min at roon temperature. Without any washing procedure, the cells were stained by $[TPE\text{-}Dim\text{-}DMe]^{2+}[Br]_2^{2-}$. The bright field and fluorescence images were acquired with Olympus laser scanning confocal microscope (FV3000).

4,4'-(2,2-diphenylethene-1,1-diyl)bis(methylbenzene) (**1**)

Diphenylmethanone (3 g, 14.27 mmol) , 4,4-dimethylbenzophenone (2.6 g, 14.27 mmol) and a Zn-dust (2.8 g, 42.81 mmol) were added into a 250 mL double-neck flack under N_2 atmosphere,100 mL THF was added in the flack, then $TiCl_4$ (5 mL)was added dropwise at -10 ^oC, The mixture was stirred at room temperature for 10 min and refluxed at 85 ^oC for 12h further. After cooling, THF was evaporated in vacuo and the crude product was extracted with dichloromethane, the organic phase was wash with water and dried with $MgSO_4$. Then Silica-gel column

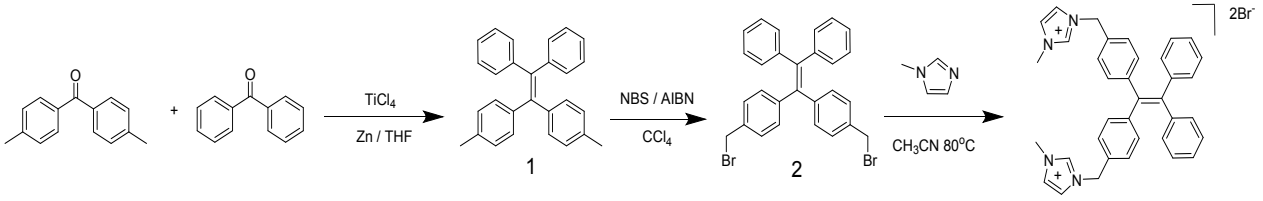
purification (n-hexane was used as eluent) solution afforded white 4,4'-(2,2-diphenylethene-1,1-diyl)bis(methylbenzene) powder with 80 % reaction yield. ^{1}H NMR ($CDCl_3$, δ, ppm) 7.14-7.06 (m, 6H), 7.05-6.99 (m, 4H), 6.89 (dd, *J* =21.08 Hz, 8H), 2.24 (s, 6H).

4,4'-(2,2-diphenylethene-1,1-diyl)bis((bromomethyl)benzene) (**2**)

Compound **1** (1.5 g, 4.16 mmol), NBS (1.48 g, 8.33 mmol) and AIBN (30 mg) were refluxed in CCl_4 under N_2 atmosphere for 12 h. After cooling and filtering, the filtrate was evaporated and purified by column chromatography (n-hexane: CH_2Cl_2 = 6:1 solution was used as eluent). Yield, 50%. ^{1}H NMR ($CDCl_3$, δ, ppm) 7.16-7.06 (m, 10H), 7.03-6.94 (m, 8H), 4.40 (s, 4H).

[TPE-Dim-DMe] $(Br)_2$

Compound **2** (0.2 g, 0.38 mmol), 1-methylimidazole (0.073 mL, 0.926 mmol) and 20 mL acetonitrile were added into a 100 mL flack with stirrer. The mixture was stirred at 78 ^{o}C for 12 h. After cooling of the reaction, acetonitrile was evaporated to dryness under reduced pressure. The crude was washed with cold methanol and dried in vacuo. Yield, 92%. ^{1}H NMR ($CDCl_3$, δ, ppm) 9.26 (s, 2H), 7.71 (d, *J* = 1.5 Hz, 4H), 7.16 (d, *J* = 8.2 Hz, 4H), 7.08 (dd, *J* = 8.8, 4.0 Hz, 6H), 6.98 – 6.89 (m, 8H), 5.33 (s, 4H), 3.82 (s, 6H). ^{13}C NMR (101 MHz,) δ 143.80 (s), 143.28 (s), 139.63 (s), 137.27 (s), 133.63 (s), 131.60 (s), 131.04 (s), 128.45 (s), 128.17 (s), 127.35 (s), 124.58 (s), 122.81 (s), 51.88 (s), 36.45 (s). ESI-MS: calcd. for [TPE-Dim-DMe]$^{2+}$], 261.1385; found, 213.1386.



Scheme S1 Synthesis of **[TPE-Dim-DMe] $(Br)_2$.**

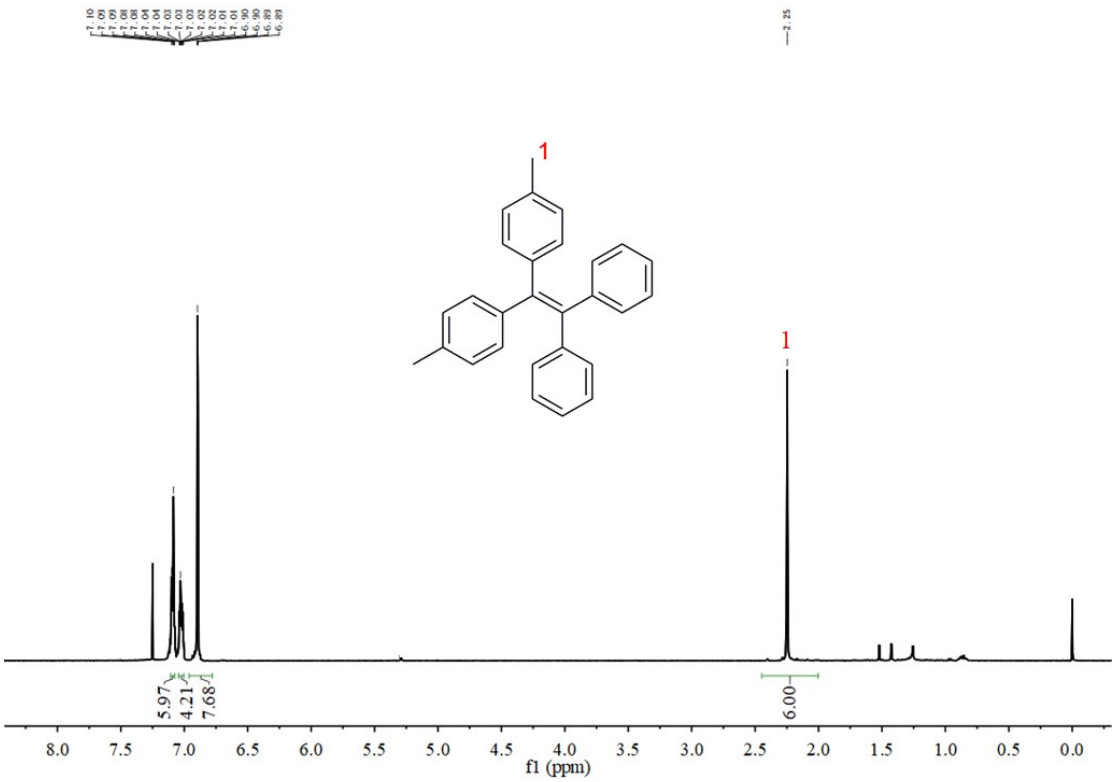


Figure S1. ^{1}H NMR spectra (400MHz, $CDCl_3$) of **1**

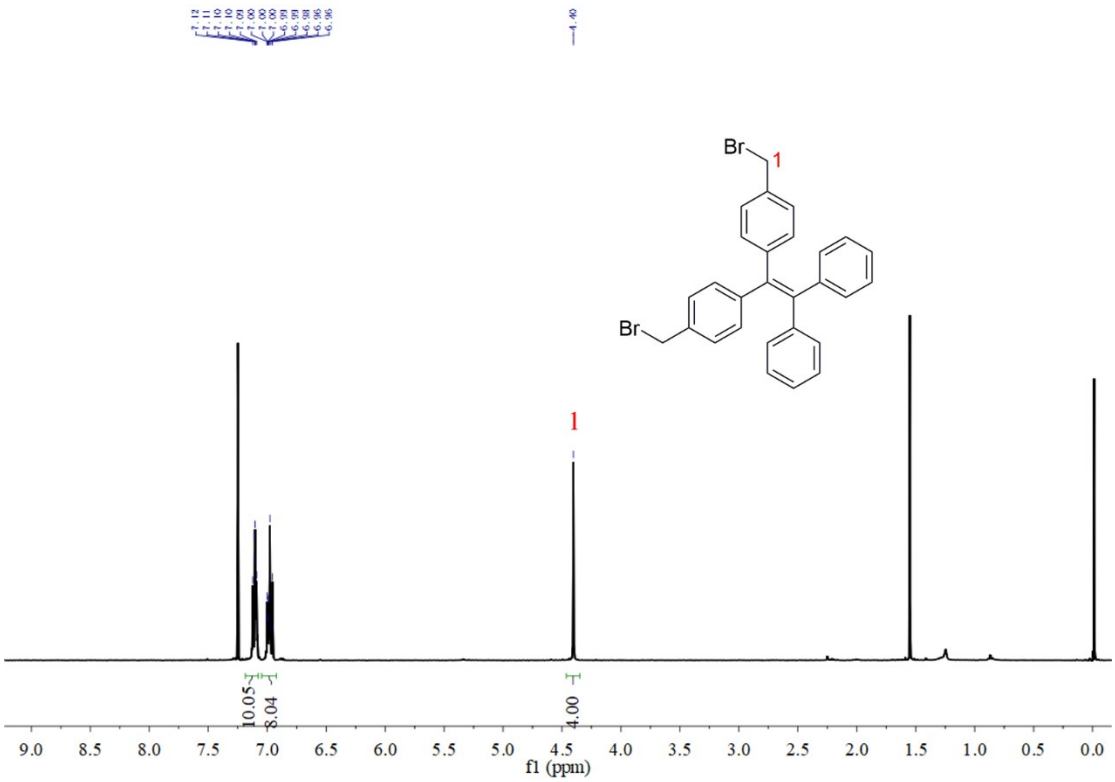


Figure S2. ^{1}H NMR spectra (400 MHz, $CDCl_3$) of **2**

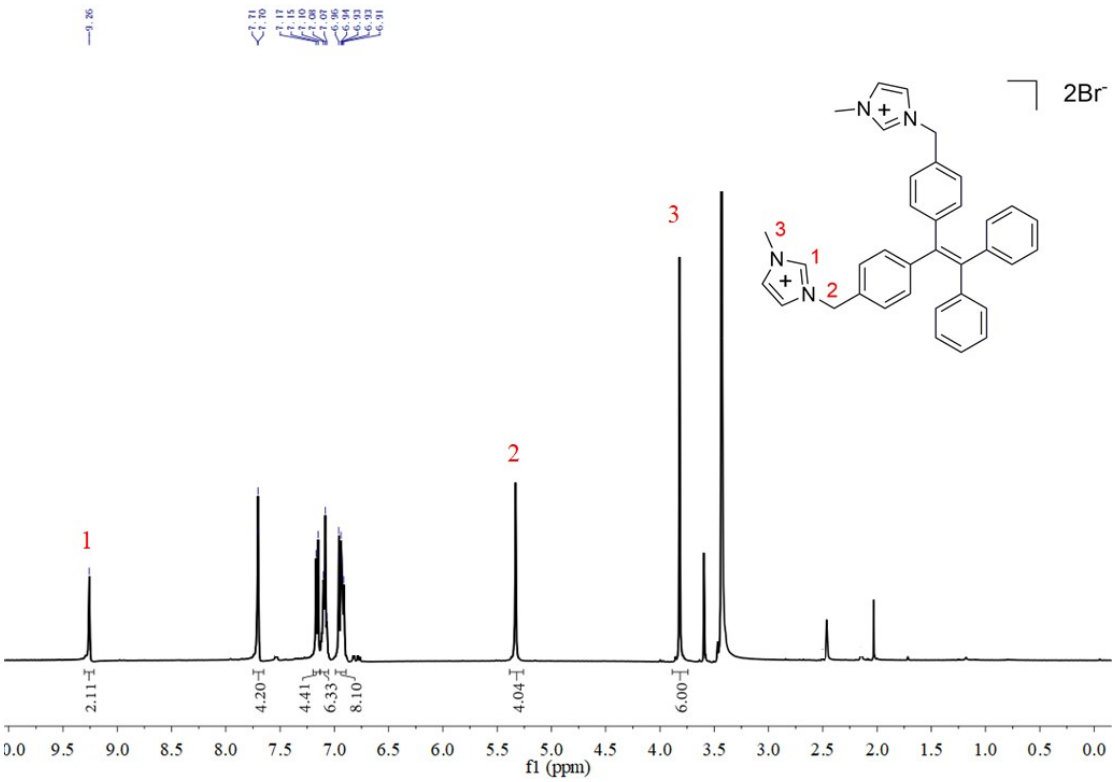


Figure S3. ^{1}H NMR spectra (400 MHz, DMSO-*d6*) of **[TPE-Dim-DMe] $(Br)_2$**

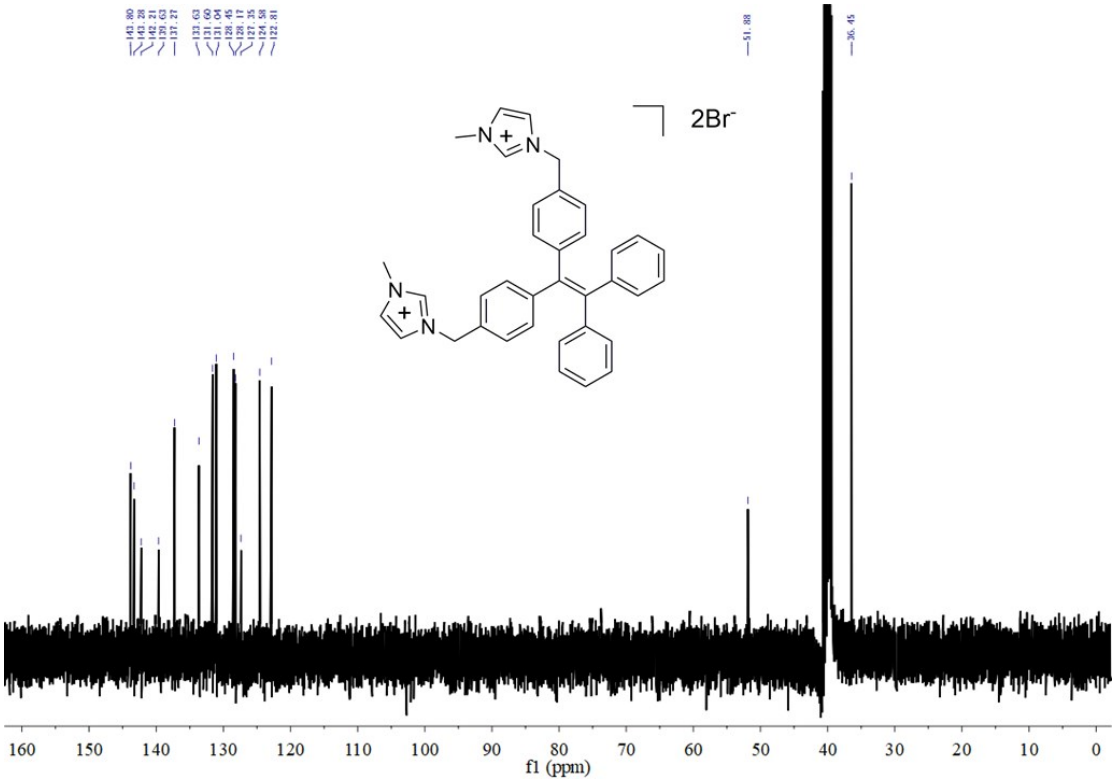


Figure S4. ^{13}C NMR spectra (100 MHz, DMSO-*d6*) of **[TPE-Dim-DMe] $(Br)_2$**

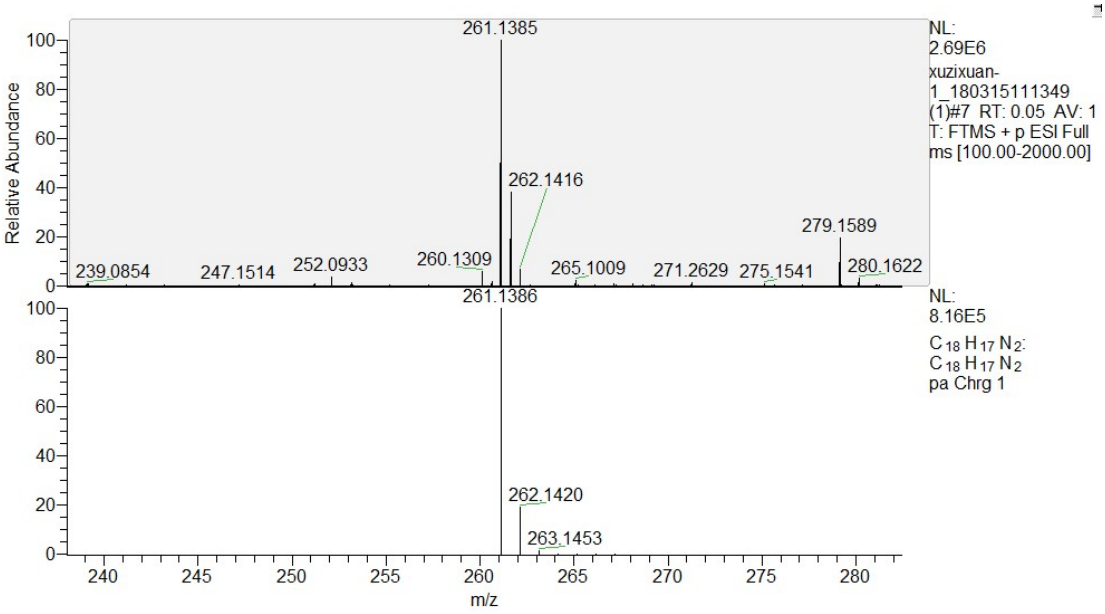


Figure S5. HR-ESI-MS of **[TPE-Dim-DMe] $(Br)_2$**.

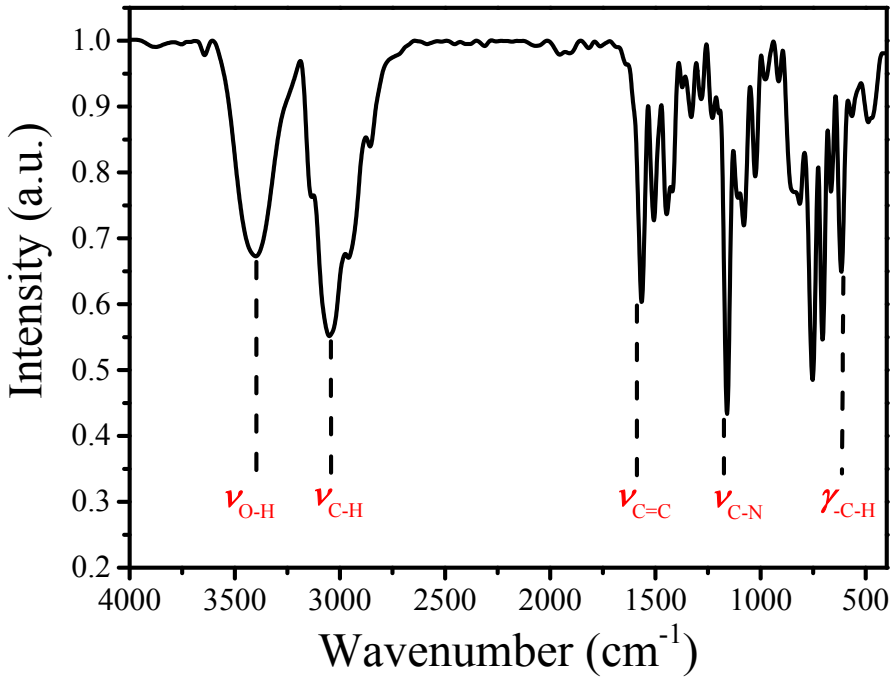


Figure S6. The FT-IR spectra of **[TPE-Dim-DMe] $(Br)_2$**

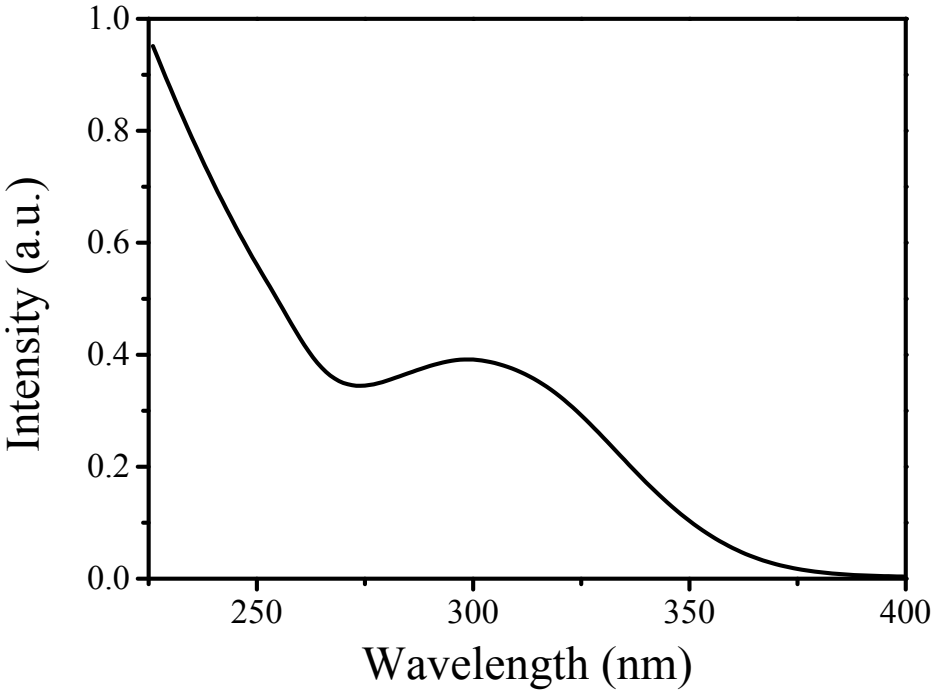


Fig S7. The UV-vis absorption spectra of **[TPE-Dim-DMe] $(Br)_2$** (10 μM) in CH_3CN

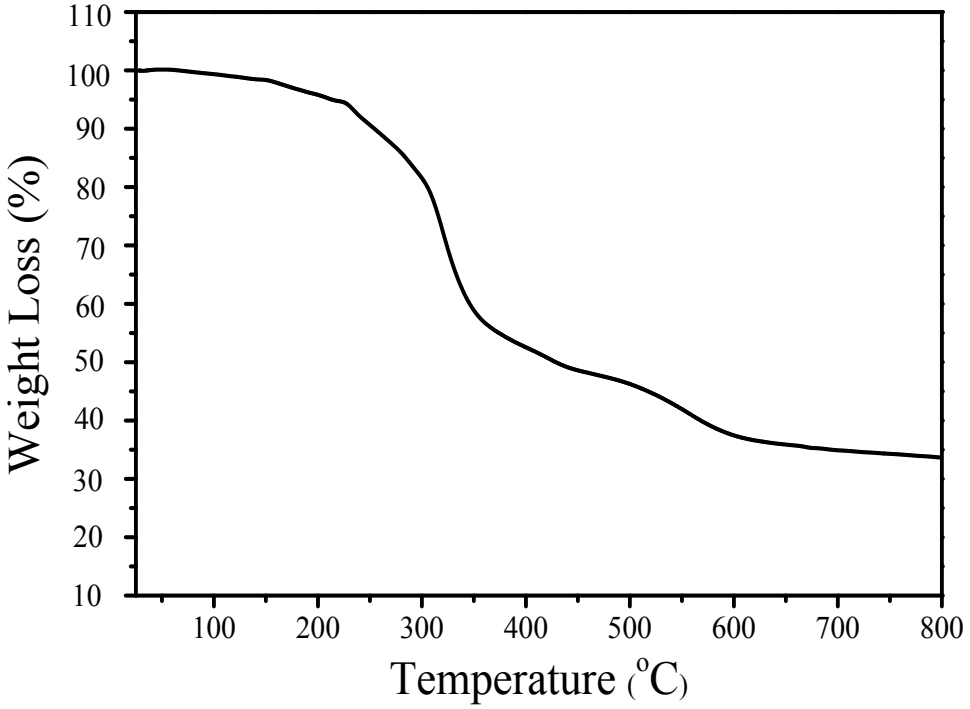
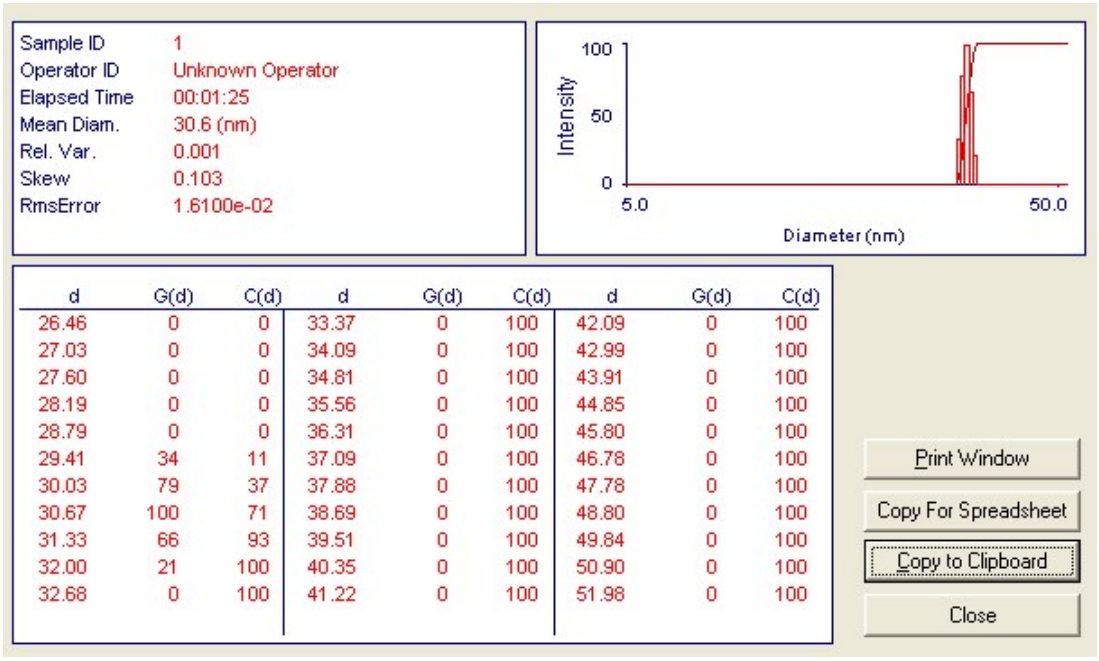


Fig S8. Thermo-gravimetric analyses (TGA) of **[TPE-Dim-DMe] $(Br)_2$**



d	G(d)	C(d)	d	G(d)	C(d)	d	G(d)	C(d)
26.46	0	0	33.37	0	100	42.09	0	100
27.03	0	0	34.09	0	100	42.99	0	100
27.60	0	0	34.81	0	100	43.91	0	100
28.19	0	0	35.56	0	100	44.85	0	100
28.79	0	0	36.31	0	100	45.80	0	100
29.41	34	11	37.09	0	100	46.78	0	100
30.03	79	37	37.88	0	100	47.78	0	100
30.67	100	71	38.69	0	100	48.80	0	100
31.33	66	93	39.51	0	100	49.84	0	100
32.00	21	100	40.35	0	100	50.90	0	100
32.68	0	100	41.22	0	100	51.98	0	100

Fig S9. DLS of **[TPE-Dim-DMe] $(Br)_2$** (0.5 mM) in water

Table S1 Crystallographic data for **[TPE-Dim-DMe] $(Br)_2^-$**

Crystal data and structure refinement for $[TPE\text{-}Dim\text{-}DMe]^{2+}[Br]_2^{2-}$		
Identification code	$[TPE\text{-}Dim\text{-}DMe]^{2+}[Br]_2^{2-}2H_2O$	
Empirical formula	$C_{36}H_{34}Br_2N_4$	
Formula weight	718.50	
Temperature	293 K	
Wavelength	1.54184 Å	
Crystal system	monoclinic	
Space group	P 21/c	
Unit cell dimensions	a=8.30793(16)	
	b=15.8271(3)	α = 90 °
	c=25.9265(7)	β=92.478 °(2)
Volume	3405.9(13)	γ = 90 °
Z	4	
Density (calculated)	1.844 Mg/m^3	
Absorption coefficient	5.845 mm^{-1}	
F (000)	1472.0	
Crystal size	0.16×0.14×0.12 mm^3	
The range for data collection	5.31 to 69.4°	
Index ranges	-5≤ h ≤9, -18≤ k ≤17, -30≤ k ≤30	
Reflections collected	13185	
Independent reflections	5976 (R_{int} = 0.0286)	
Completeness to theta=66.97	99.87	
Absorption correction	multi-scan	
Refinement method	Full-matrix least-squares on F2	
Data / restraints /parameters	/0/415	
Goodness-of-fit on F^2	1.181	
Final R indices [I > 2σ(I)]	R1=0.0725, wR2=0.1750	
R indices (all data)	R1=0.0785, wR2=0.1770	

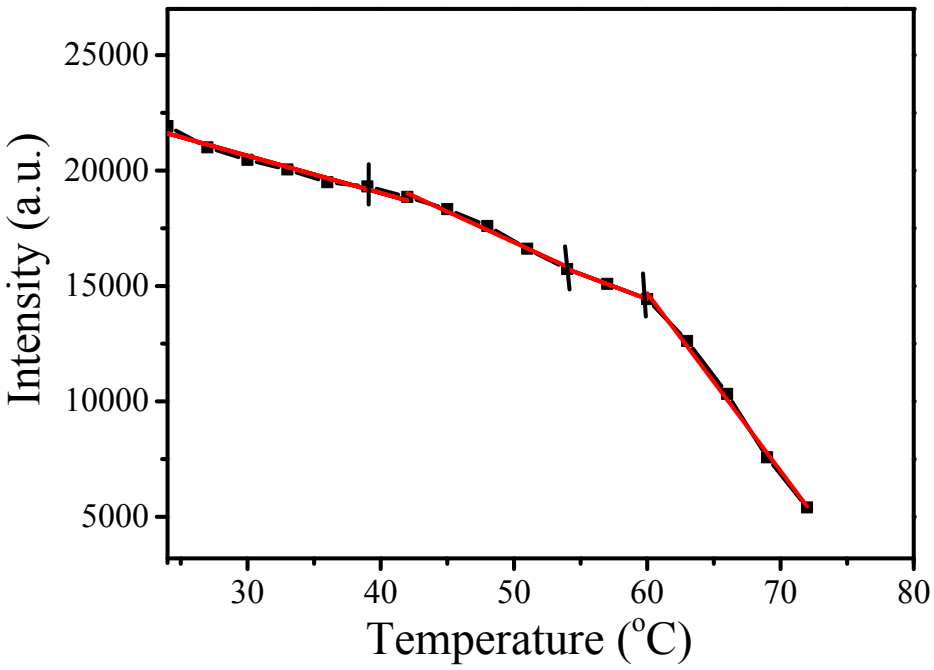


Fig S10. The effect of the temperatures on fluorescent intensity of **[TPE-Dim-DMe] $(Br)_2$** crystal.

Table S2 The data of linear relationship between temperatures and fluorescent intensity of **[TPE-Dim-DMe] $(Br)_2$** crystal.

24- 42 °C			
Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	231343		
Pearson's r	-0.98285		
Adj. R-Square	0.9592		
		Value	Standard Error
Book1_B	Intercept	25485.5	454.4846
Book1_B	Slope	-161.5	13.55011
42-56 °C			
Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	77145.9		
Pearson's r	-0.99397		
Adj. R-Square	0.98397		
		Value	Standard Error
Book1_B	Intercept	30165.6	814.52731
Book1_B	Slope	-265.43333	16.90342
56-60 °C			
Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	112.66667		
Pearson's r	-0.99993		
Adj. R-Square	0.99973		
		Value	Standard Error
Book1_B	Intercept	27415.33333	142.73713
Book1_B	Slope	-216.33333	2.50185
60-72 °C			
Equation	y = a + b*x		

Weight	No Weighting		
Residual Sum of Squares	225198.679		
Pearson's r	-0.99789		
Adj. R-Square	0.99439		
		Value	Standard Error
Book1_B	Intercept	60871.84	1910.03105
Book1_B	Slope	-769.71	28.88026

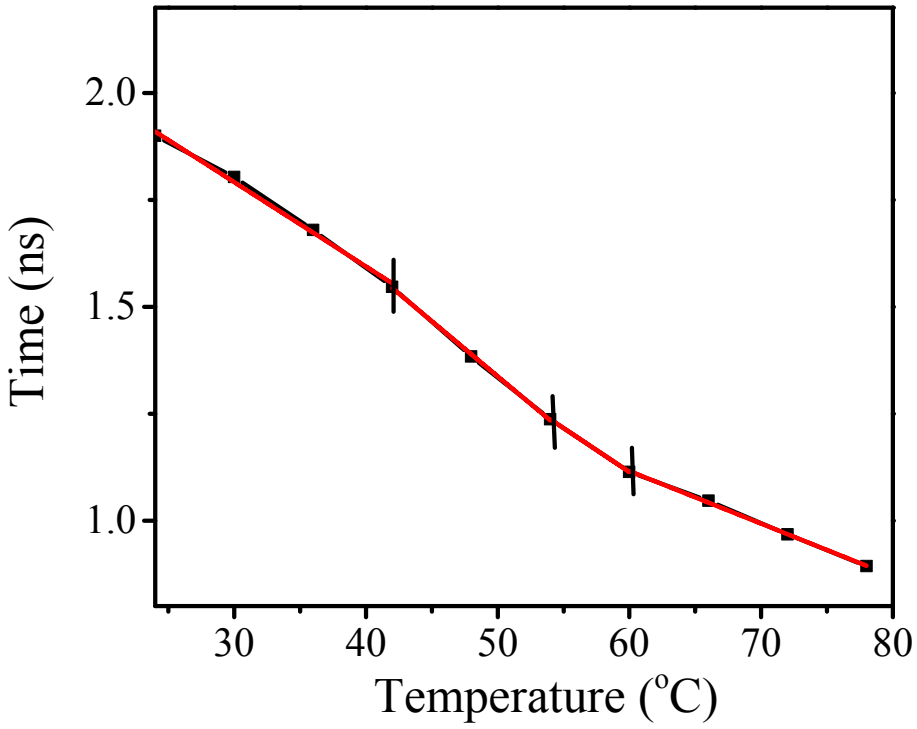


Fig S11. The effect of the temperatures on PL decay time of **[TPE-Dim-DMe] $(Br)_2$** crystal.

Table S3 The data of linear relationship between temperatures and PL decay time of **[TPE-Dim-DMe] $(Br)_2$** crystal.

24- 42 °C			
Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	3.53352E-4		
Pearson's r	-0.99749		
Adj. R-Square	0.99247		
		Value	Standard Error
B	Intercept	2.38342	0.03336
B	Slope	-0.01972	9.90724E-4
42-56 °C			
Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	4.81667E-5		
Pearson's r	-0.9995		
Adj. R-Square	0.99799		
		Value	Standard Error
B	Intercept	2.62747	0.03946
B	Slope	-0.0258	8.17913E-4
56-60 °C			
Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	0		
Pearson's r	-1		
Adj. R-Square	--		
		Value	Standard Error
B	Intercept	2.34923	--
B	Slope	-0.0206	--
60-78 °C			

Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	2.34411E-5		
Pearson's r	-0.99957		
Adj. R-Square	0.99871		
		Value	Standard Error
B	Intercept	1.85428	0.01769
B	Slope	-0.01231	2.55175E-4