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Turn-On Fluorescent Probe with Aggregation-Induced Emission Characteristic for Polyazoles

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1. Materials and Methods

1.1 Experimental Materials

E,E-HPB-CHO was prepared according to our previous reported method[1]. 1,3-Indanedione was purchased from J&K Scientific Ltd. Other chemical reagents were purchased from Aladdin Industrial Inc. All chemicals were used without further purification.

1.2 Instrumentations and Methods

The UV-vis spectra were recorded on a TU-1901 UV-Vis spectrophotometer (Beijing Purkinje General Instrument Co., Ltd.). Photoluminescence (PL) spectra were collected on a Hitachi F-7000 fluorescence spectrophotometer at room temperature. Infrared spectra were recorded on a Bruker Alpha spectrometer. The nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AMX-400 spectrometer using deuterated chloroform, THF or mixture of THF/water as the solvent. Fluorescence quantum yield (QY) were collected on an Inregrating sphere mounted directly in sample compartemt of Fluorometer (HORIBA Scientific, NanoLog, with F-3018 integrating spjere, Edision, USA). The excitiation wavelength was 410 nm. Scanning electron microscope (SEM) images were collected on S4800 with 5.0 KV. Transmission electron microscope (TEM) images were recorded on a JEOL 2100F.

1.3 Theoretical calculations

Computational studies were carried out by using Gaussian09 with B3LYP/6-31 G(d,p) method (isovalue is 0.02).

*1.4 Synthesis of **E,E-HPB-ID**.*

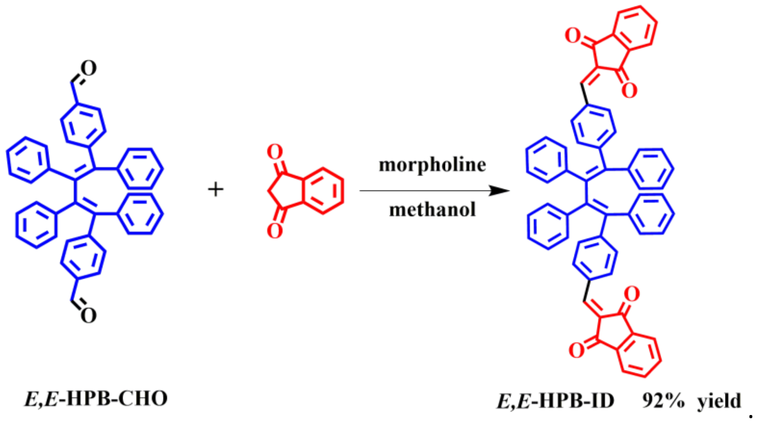


Figure. S1 Synthetic route of ***E,E*-HPB-ID**.

A mixture of ***E,E*-HPB-CHO** (1.00 mmol, 566 mg) and 1,3-Indanedione (2.00 mmol, 1024 mg) in methanol (2.5 mL) was stirred at 45 °C for 2h and then filtered to remove catalyzer. A orange-red solid was obtained by recrystallization and dried under vacuum for 24 h (750 mg, 92% yield). ^{1}H-NMR (400 MHz, *THF-d8*). δ (ppm) 8.76 (d, 2H), 8.33 (d, 2H), 8.04-7.82 (m, 12H), 7.72 (s, 2H), 7.27-6.86 (m, 20H), ^{13}C-NMR (100 MHz, $CDCl_3$) δ (ppm) 189.04, 149.81, 146.35, 142.87, 142.55, 140.95, 139.99, 135.31, 135.04, 133.71, 131.97, 131.33, 130.12, 128.52. 127.64, 127.20, 126.78, 123.26. MS (MALDI-TOF, m/z): calcd for $C_{60}H_{38}O_4$: 822; found 822.35 and 845.34 (with Na^+).

1.5 Methods for the Preparation of Sample.

Sample for detection of polyazoles

The concentration of ***E*,*E*-HPB-ID** was 1×10^{-4} mol/L in THF/water mixture, because particle size of ***E*,*E*-HPB-ID** in THF/water mixture with a water fration of 90% is 79.3 nm in the concertration of 1×10^{-5} mol/L, which showed no fluoresent response to NTO.

Samples for TEM and SEM: ***E*,*E*-HPB-ID** (1×10^{-4} mol/L in 90% water fration THF/water mixture), NTO (1×10^{-2} mol/L in 90% water fration THF/water mixture) and mixture of ***E*,*E*-HPB-ID** and NTO ($M_{\boldsymbol{E,E}\textbf{-HPB-ID}}$: M_{NTO}= 1:2, 1×10^{-4} mol/L in 90% water fration THF/water mixture) were freeze-dried by using vacuum freeze dryer to obtain powder.

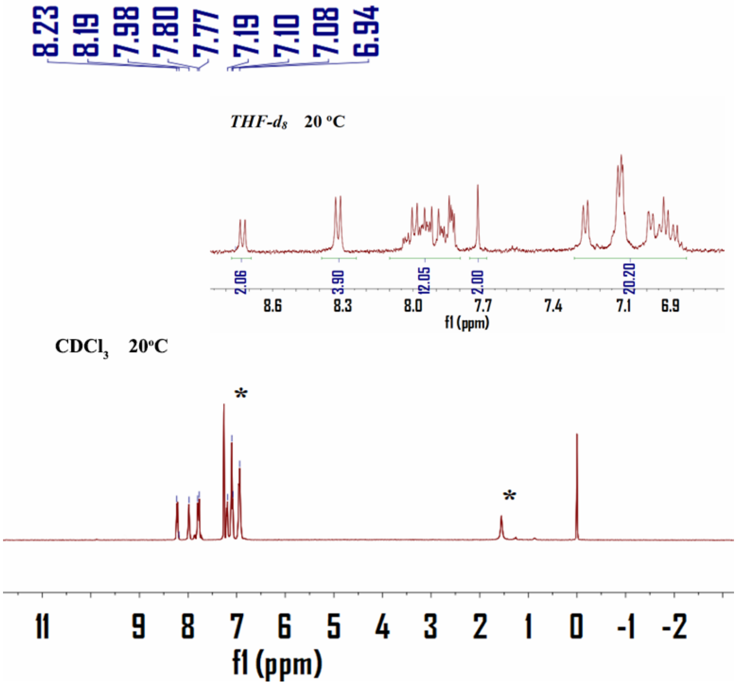


Figure. S2 ^{1}H-NMR spectra of ***E*,*E*-HPB-ID**.

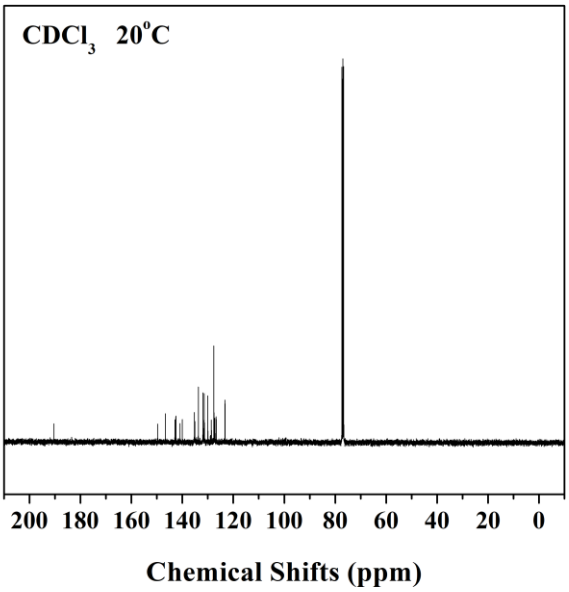


Figure. S3 ^{13}C-NMR spectra of ***E,E*-HPB-ID** in deuterated chloroform.

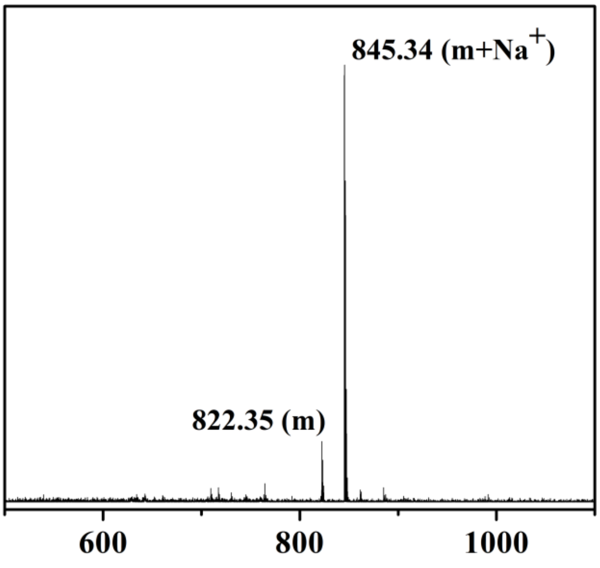


Figure S4. MS of ***E,E*-HPB-ID**.

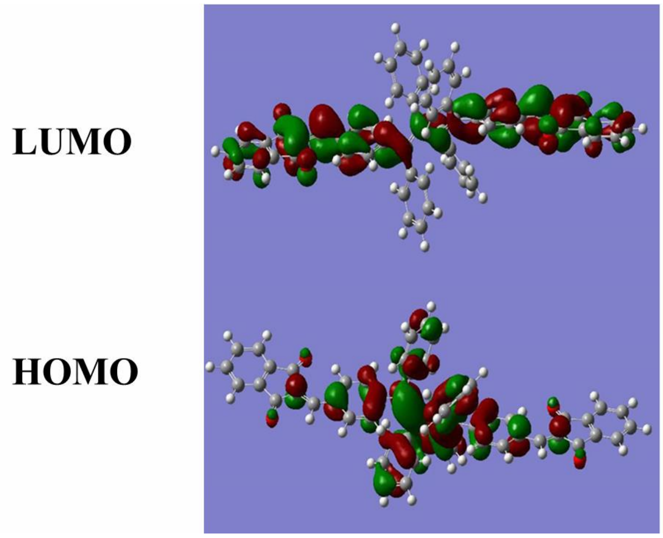


Figure S5. B3LYP/6-31G (d) calculated molecular orbital of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels of ***E*,*E*-HPB-ID**.

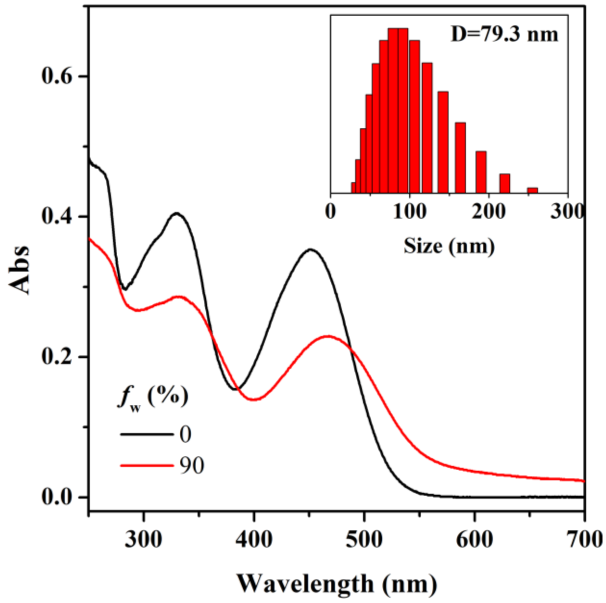


Figure S6. Absorption spectra of different water fraction of ***E*,*E*-HPB-ID**; Inset: Dynamic light scattering results of ***E*,*E*-HPB-ID** in 90% water fraction [***E*,*E*-HPB-ID**] = 1×10^{-5} mol/L.

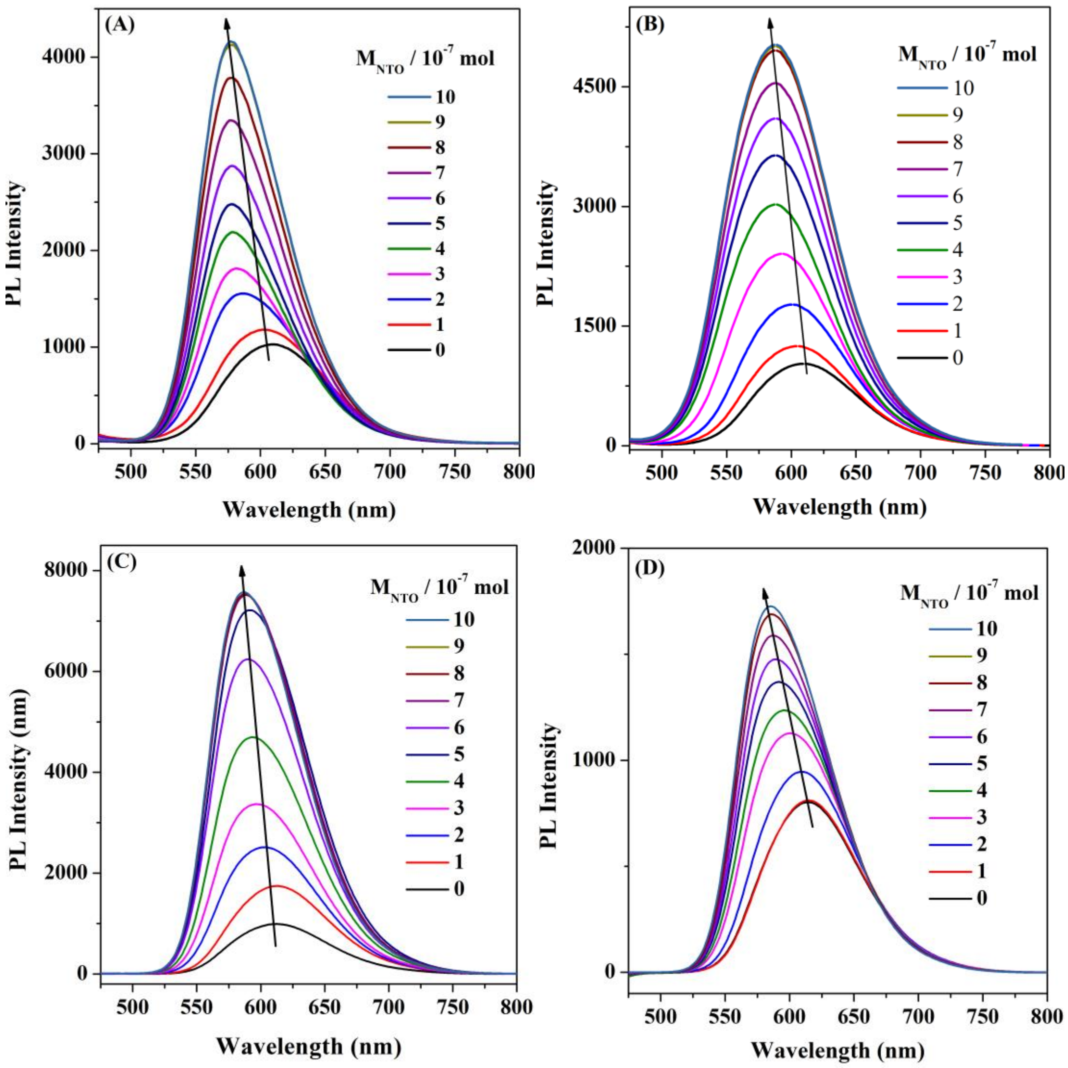


Figure S7 Fluorescence spectra of different sizes of ***E,E*-HPB-ID** in 90% water fraction upon addition of NTO solution.

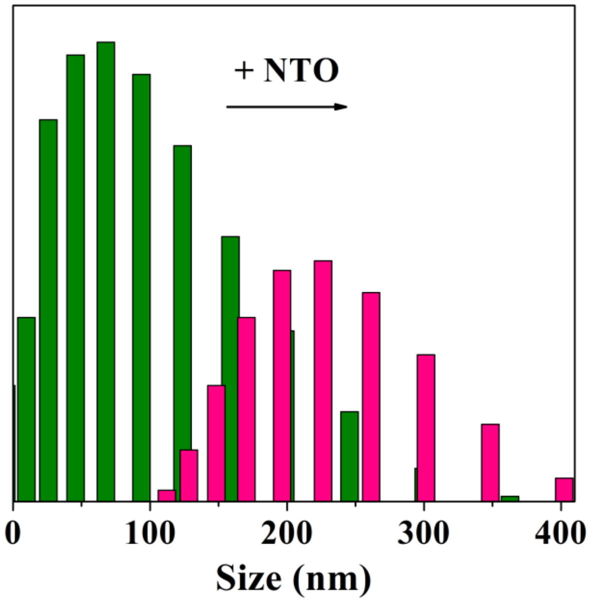
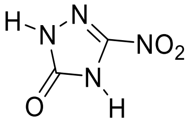
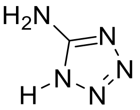
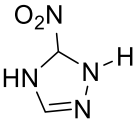
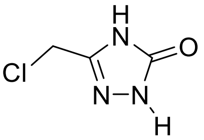
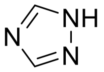
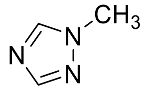
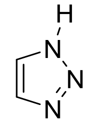
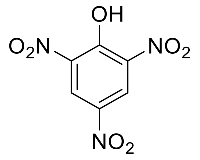
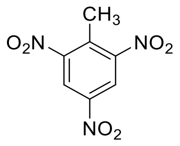
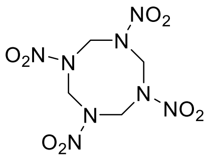
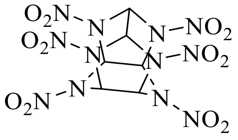
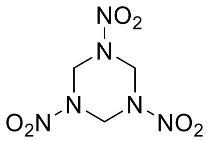
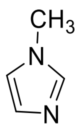
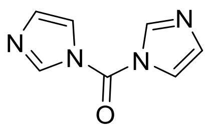
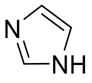
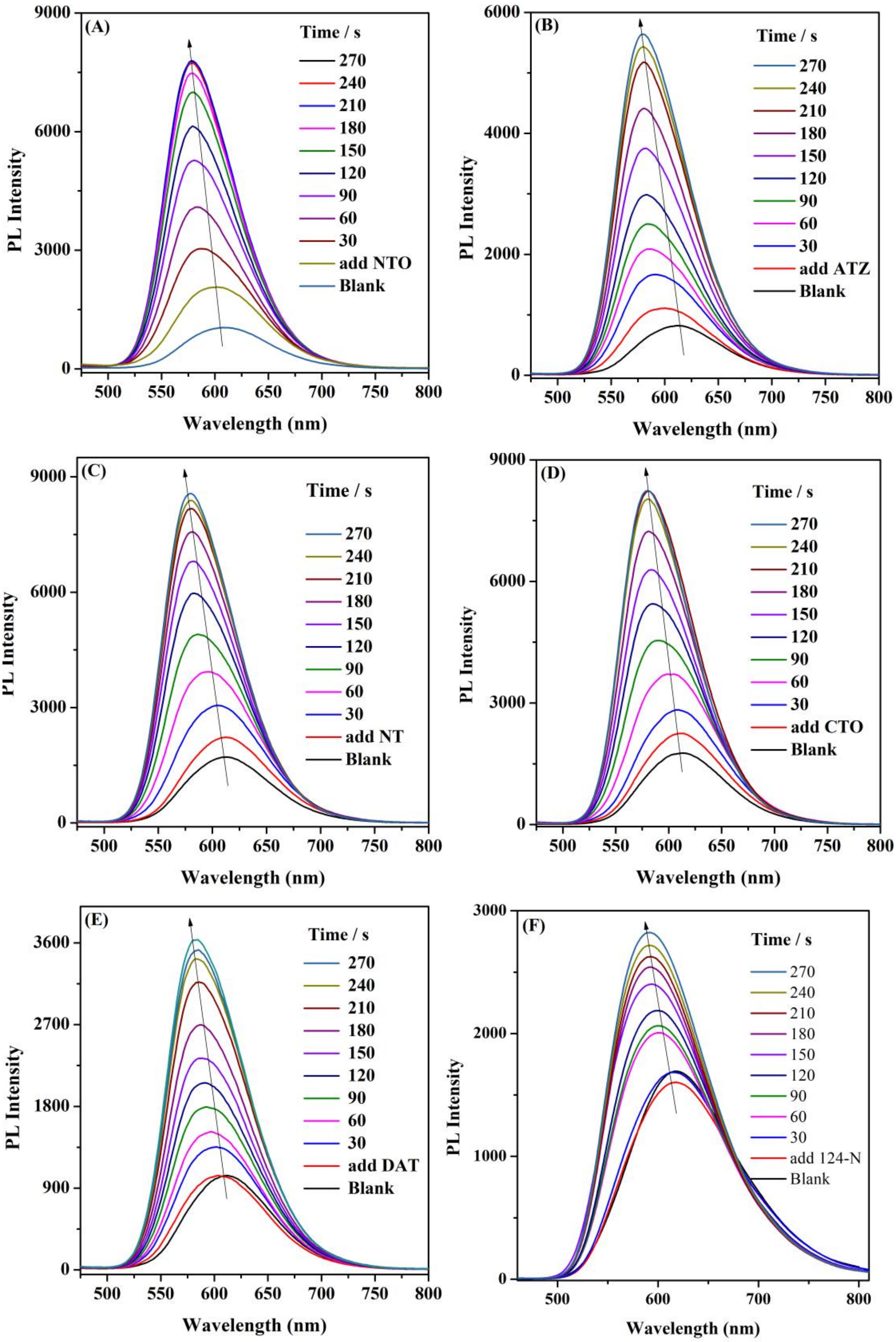


Figure S8. Dynamic light scattering results of ***E,E*-HPB-ID** at 90% water fraction of 74 nm particle size before and after addition of NTO (1×10^{-6} mol).

Table S1. The name, shortened form of name and structure of analytes.

Name	Shortened form	Structure
5-nitro-2,4-dihydro-3H-1,2,4-triazole-3-one	NTO	
5-amino-1H-tetrazole	ATZ	
3-Nitro-1,2,4-triazole	DT	
5-(chloromethyl)-2,4-dihydro-3H-1,2,4-triazol-3-one	CTO	
1,2,4-Triazole	1,2,4-N	

1-methyl-1H-1,2,4-triazole	1,2,4-N-1	
1H-1,2,3-triazole	1,2,3-N	
Picric acid	PA	
2,4,6-Trinitrotoluene	TNT	
Cyclotetramethylenete-tranitramine	HMX	
2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazatetracyclo[5.5.0.0.0]dodecane	CL-20	
1,3,5-trinitroperhydro-1,3,5-triazine	RDX	
1-methyl-1H-imidazole	N-IM	
Di(1H-imidazol-1-yl)methanone	2N-IM	
1H-imidazole	IM	


(A)
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add NTO
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PL Intensity
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(B)
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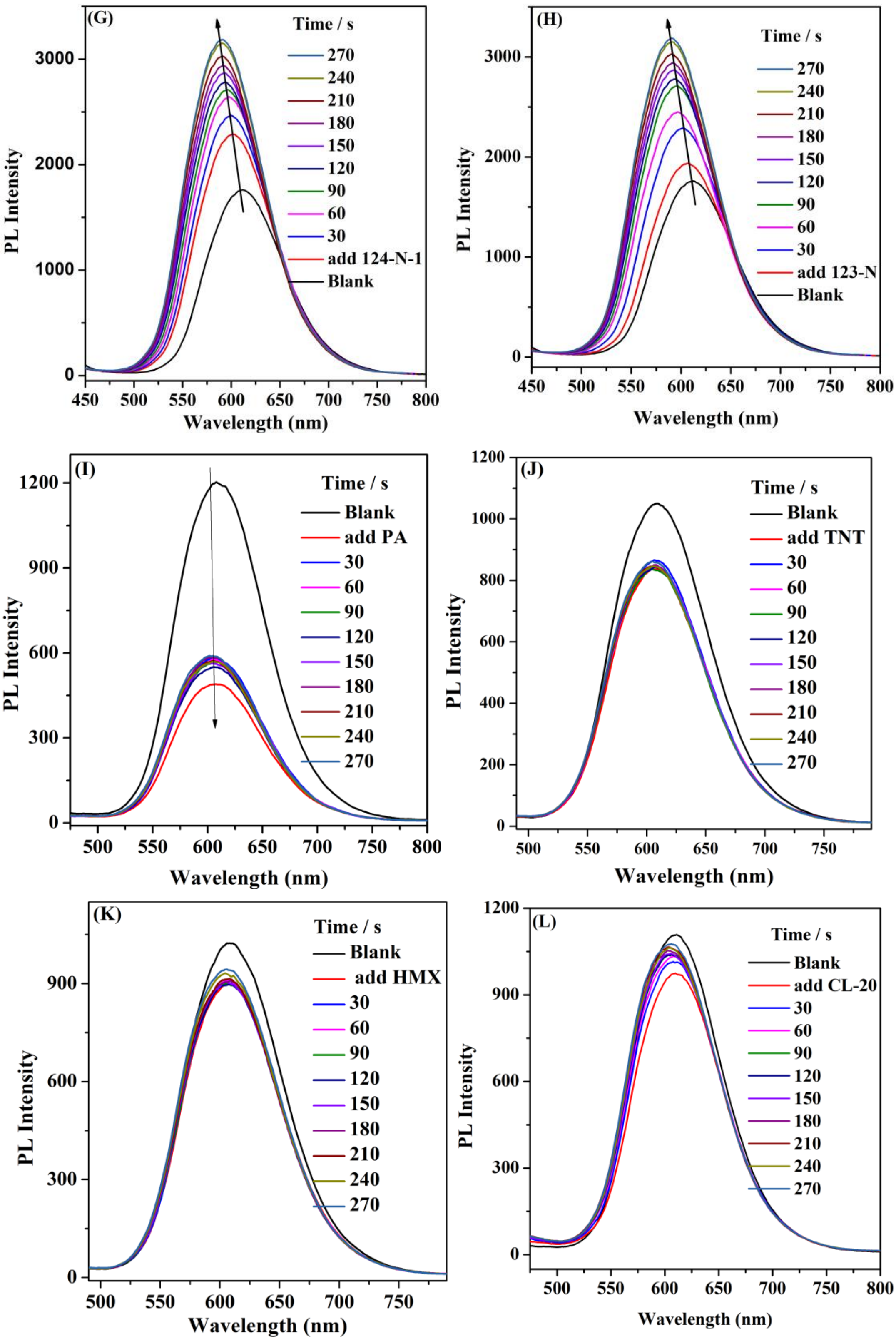
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Wavelength (nm)
(H)
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add 123-N
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PL Intensity
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Wavelength (nm)
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PL Intensity
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Wavelength (nm)
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PL Intensity
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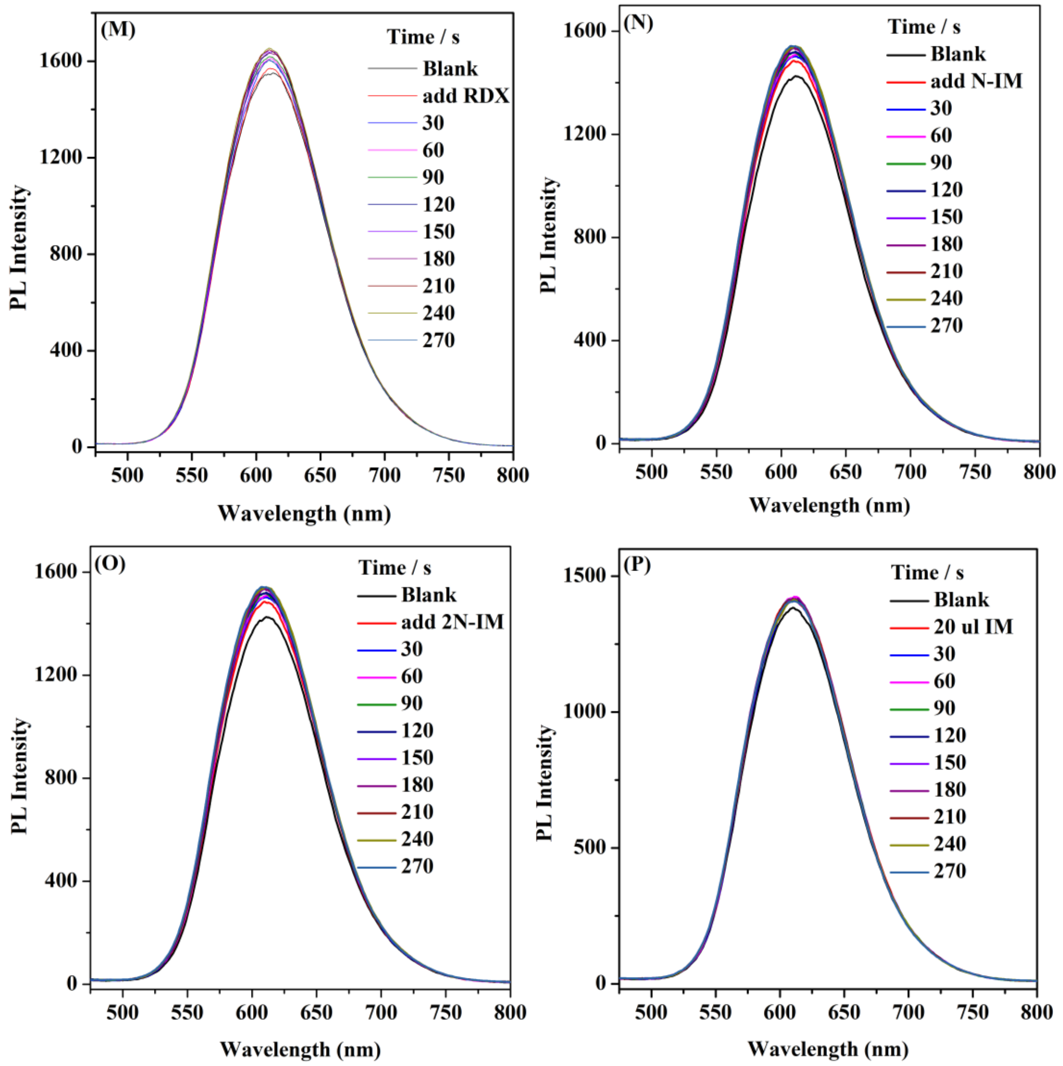

Figure S9. Fluorescence spectra of 90% water fraction ***E,E*-HPB-ID** with 1×10^{-2} mol/L, 100 μL (A)NTO, (B)ATZ, (C)NT, (D)CTO, (E)DAT, (F)124-N, (G)124-N-1, (H) 123-N, (I) PA, (J)HMX, (K) TNT, (L) CL-20, (M) RDX, (N) N-IM, (O) 2N-M and (P) IM for 270s.

Table S2. Values of Quenching Constants (K_{SV}) for analytes[a].

	PA	TNT	HMX	CL-20	RDX	N-IM	2N-IM	IM
K_{SV}	-140	-50	-40	-20	40	40	20	12

[a] [***E,E*-HPB-ID**]= 1×10^{-4} mol/L

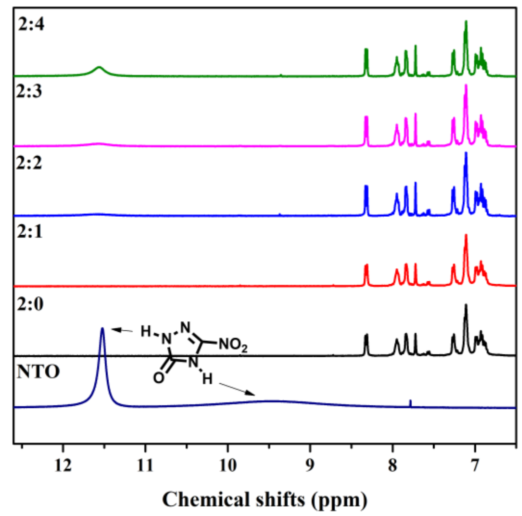

Figure S10 ^{1}H-NMR spectra of***E,E*-HPB-ID** with and without NTO in deuterated THF. $[M_{E,E\text{-HPB-ID}}:M_{NTO} = 2: x]$

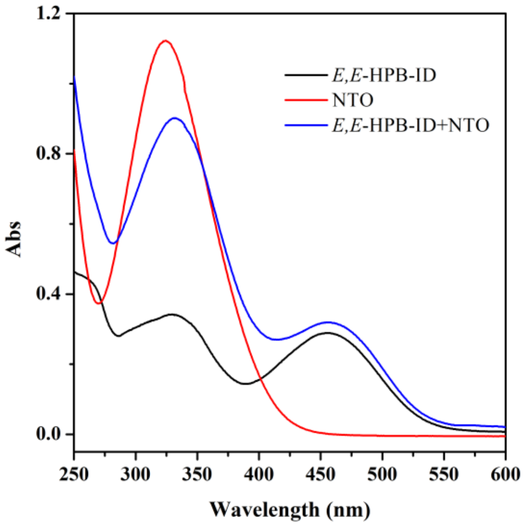

Figure S11. Absorption spectra of ***E,E*-HPB-ID**, NTO and ***E,E*-HPB-ID** +NTO. [***E,E*-HPB-ID**] = 1×10^{-4} mol/L.

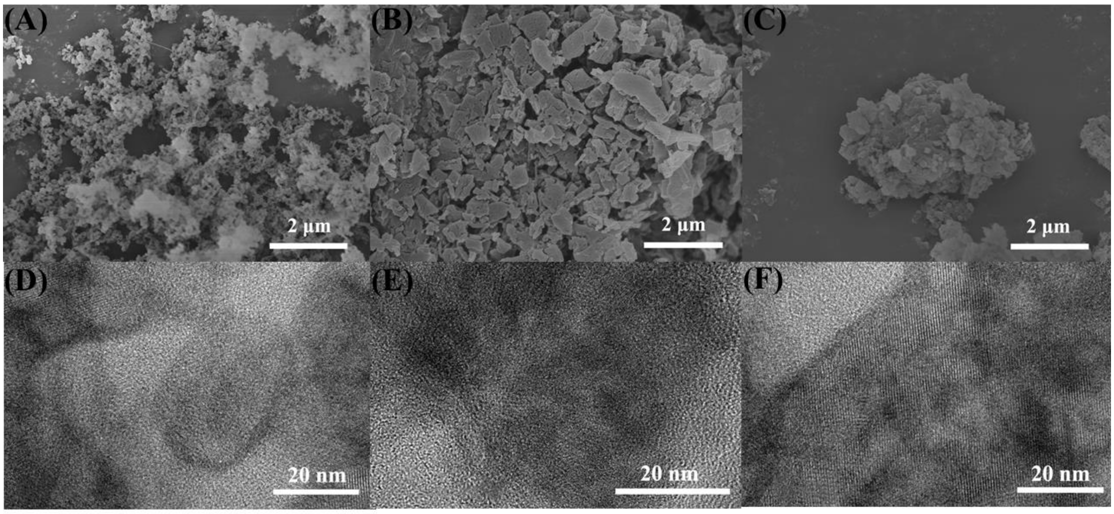

Figure S12 SEM images of (A) ***E,E*-HPB-ID**, (B) NTO and (C) ***E,E*-HPB-ID**+NTO; TEM images of (D) ***E,E*-HPB-ID**, (E) NTO and (F) ***E,E*-HPB-ID**+NTO.

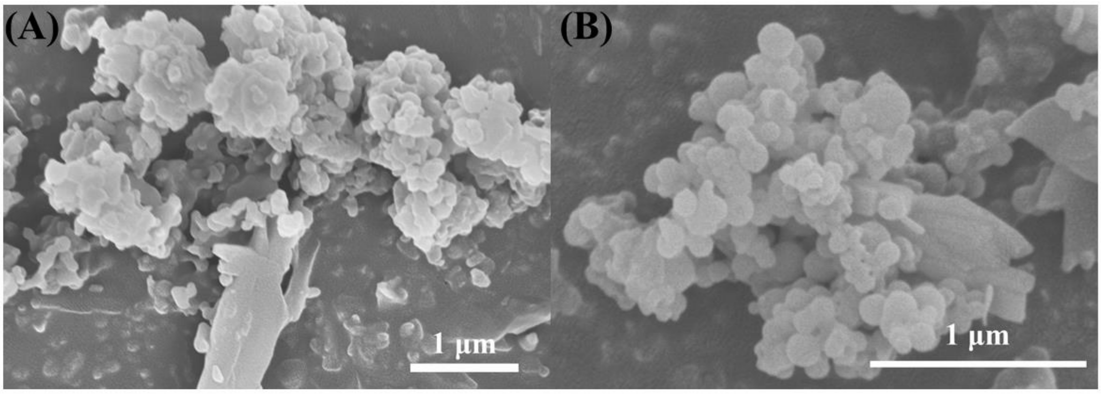

Figure S13. SEM images of ***E,E*-HPB-ID**+NTO for (A) 60 s, (B) 120 s.

REFERENCES：

Zhang, Y. H.; Mao, H. L.; Kong, L. W.; Tian, Y.; Tian, Z. L.; Zeng, X. K.; Zhi, Z. G.; Shi, J. B.; Tong, B.; Dong, Y. P. *Dyes Pigm.* **2016**, *133*, 354.