Electronic Supplementary Material (ESI) for New Journal of Chemistry

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Photoactivatable Fluorescence Enhanced Behaviour of Benzo[c][1,2,5]oxadiazole-dressing Tetraphenylethene

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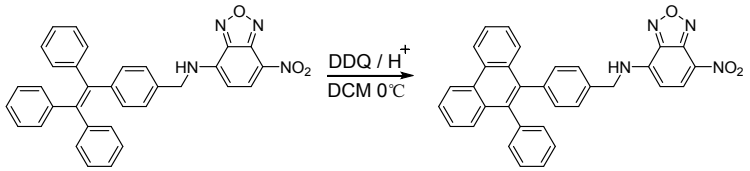
Experimental Details

Materials. All manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques, unless otherwise stated. All starting materials were obtained commercially as analytical-grade and used without further purification. **Bn-NBD** and **Bu-NBD** was synthesized according to the previous literature.[S1]

Characterizations. ^{1}H and ^{13}C NMR spectra were collected on an American Varian Mercury Plus 400 spectrometer (400 MHz). Mass spectra were recorded with the EI-MS spectrometer. UV–Vis spectra were recorded using a Hitachi U-3310 visible recording spectrophotometer. Fluorescence spectra were recorded using a Perkin Elmer LS-55. Crystal-structures of **DPP-NBD** were obtained on a Bruker APEX DUO CCD system via single crystal X-ray diffraction experiments. Absolute fluorescence quantum yields were measured on a Hamamatsu C11347 Absolute PL quantum yield spectrometer.

Single crystals of **DPP-NBD** suitable for crystallographic analysis were obtained by diffusing hexane into dichloromethane solution at room temperature. The crystal was mounted on a glass fiber for diffraction experiments. Intensity data were collected on a Nonius Kappa CCD diffractometer with Mo Kα radiation (0.71073 Å) at room temperature. The structures were solved by a combination of direct methods (SHELXS-97)[S2] and Fourier difference techniques and refined by full-matrix least-squares (SHELXL-97).[S3] All non-H atoms were refined anisotropically. The hydrogen atoms were placed in the ideal positions and refined as riding atoms.



Synthesis of DPP-NBD. TPE-NBD (100 mg, 0.19 mmol) was dissolved in dry dichloromethane (9 mL) and cooled to ~0 °C. To this solution, methanesulfonic acid (1 mL) and solid DDQ (43 mg, 0.1 mmol) were added and the resulting highly colored mixture was stirred. After 30 min, the resulting reaction mixture was quenched by pouring onto saturated aqueous $NaHCO_3$ (20 mL). The organic layer was separated and the aqueous layer was extracted with dichloromethane (2 x 10 mL). Combined organic layers were washed with water and brine, dried over anhydrous $MgSO_4$ and evaporated under vacuum to afford **DPP-NBD** which was purified by purified with column chromatography, yield: 20%. ^{1}H NMR (400 MHz, CD_3CN) δ: 8.88 (d, J = 8.0 Hz, 2H), 8.45 (d, J = 8.0 Hz, 1H), 7.81 (br, 1H), 7.70 (t, J = 6.0 Hz, 2H), 7.53 (t, J = 8.0 Hz, 2H), 7.42 (d, J = 8.0 Hz, 2H), 7.33 – 7.17 (m, 9H), 6.16 (d, J = 8.0 Hz, 1H), 4.71 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 144.38, 143.83, 143.21, 139.26, 139.14, 138.09, 136.88, 136.09, 134.50, 132.85, 132.24, 132.12, 132.03, 132.24, 131.96, 130.92, 130.36, 129.46, 129.21, 128.11, 127.71, 127.21, 126.87, 126.72, 125.59, 122.30, 121.61, 99.55, 48.56. ESI-MS: [M+H] = 523.3. Calculated exact mass: 522.5. Anal. Calcd for $C_{33}H_{22}N_4O_3$: C 75.85; H, 4.24; N, 10.72. Found: C 75.62; H, 4.31; N, 10.88.

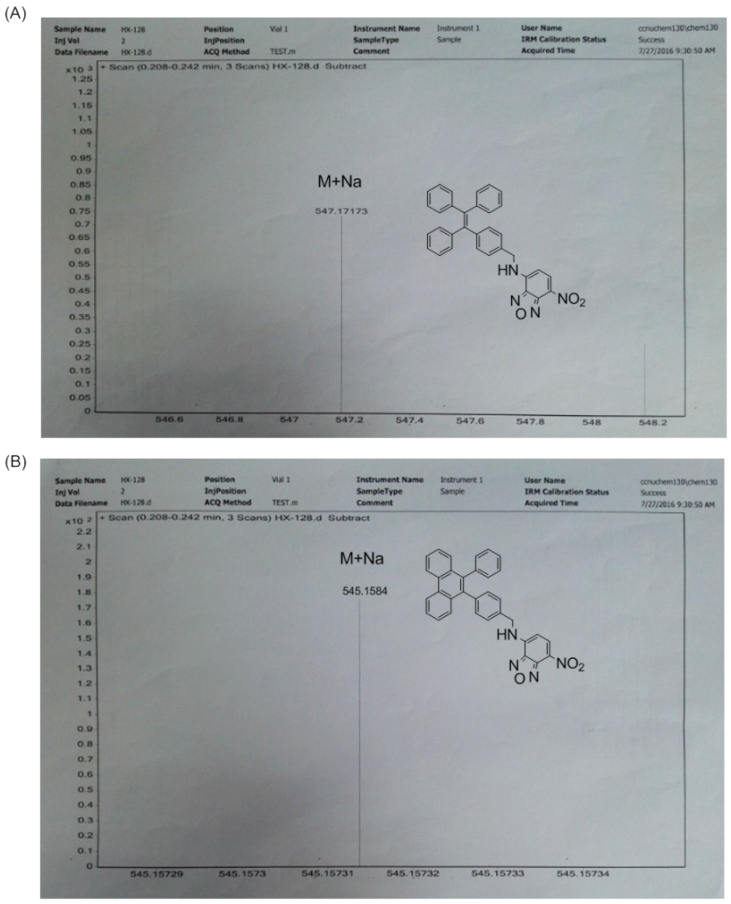


Fig. S1 HRMS spectrum of **TPE-NBD** before (A) and after (B) irradiation of UV-light (254 nm) in acetonitrile .

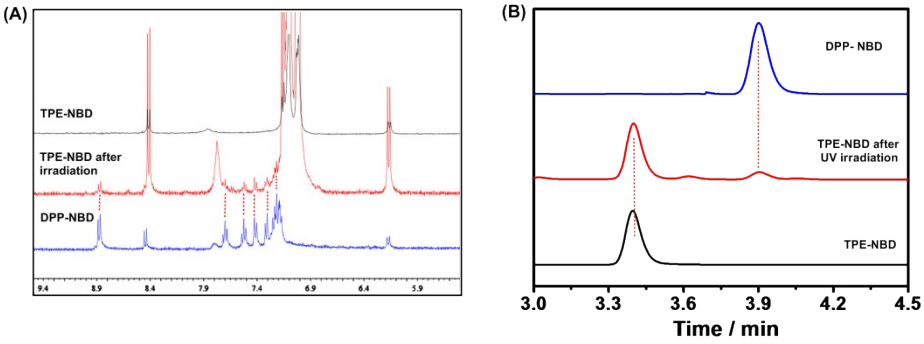


Fig. S2 ^{1}H NMR spectra (A) and HPLC analysis (B) of the photoconversion of **TPE-NBD** to **DPP-NBD** under 254 nm UV irradiation.

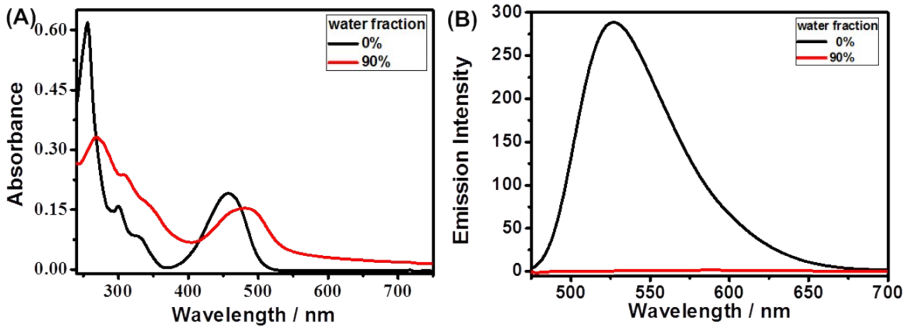


Fig. S3 Absorption (A) and fluorescence (B) spectra of **DPP-NBD** (10 μM) in the acetonitrile–water binary mixture with different water fractions (f_W). (λ_{ex} = 450 nm; Split: 15*2.5)

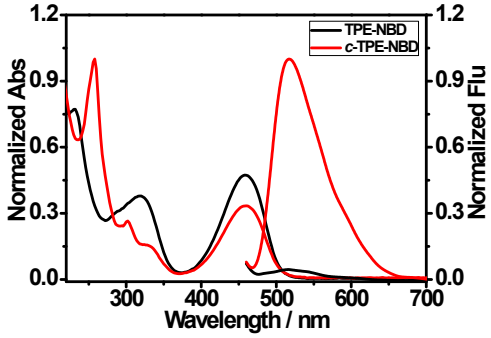


Fig. S4 Normalized absorption (A) and fluorescent (B) spectra of **TPE-NBD** and **DPP-NBD** (0.5 μM) in acetonitrile. (λ_{ex} = 450 nm; Split: 10*5)

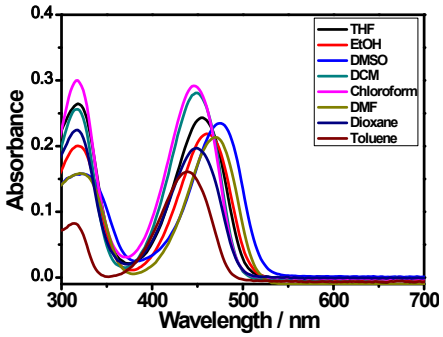


Fig. S5 Absorption of **TPE-NBD** in different solvents

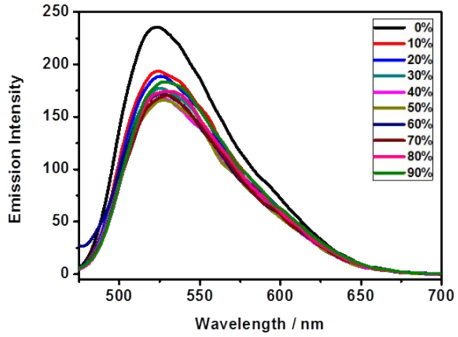


Fig. S6 Fluorescent spectra of **TPE-NBD** (10 μM; λ_{ex} = 450 nm; Slit: 10/5 nm) in the binary mixture of ethanol–glycerin with different glycerin fractions

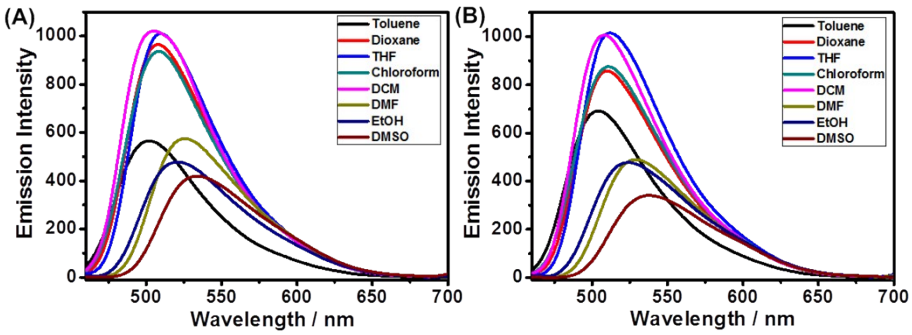


Fig. S7 Fluorescence spectra of **of NBD-Bn** (A)**, NBD-Bu** (B) in different solvents (10 μM, λ_{ex} = 450 nm; Split: 15*2.5).

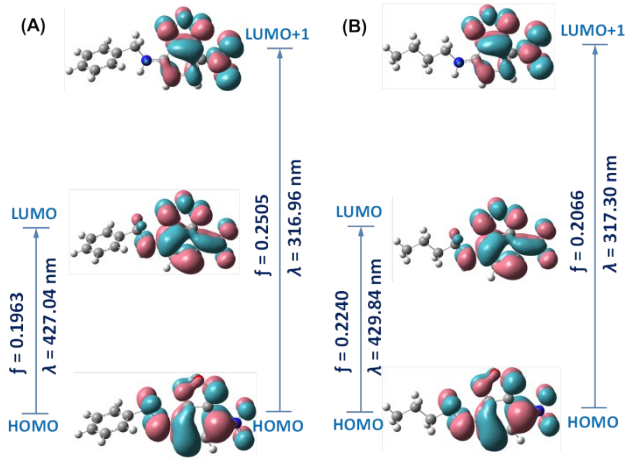


Fig. S8 Frontier molecular orbital profiles of **Bn-NBD** (A) and **Bu-NBD** (B) based on TDDFT (B3LYP/6-31G*).

Table S1. Crystal data and structure refinement parameters of **DPP-NBD.**

Compound	**DPP-NBD**	
Empirical formula	C33H22N4O3	
Formula weight	522.54	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 14.304(3) Å	α= 90
	b = 12.424(2) Å	β= 106.360(3)
	c = 15.281(3) Å	γ = 90
Volume	2605.8(8) $Å^3$	
Z	4	
Density (calculated)	1.332 Mg/m^3	
Absorption coefficient	0.087 mm^{-1}	
F(000)	1088	
Crystal size	0.150 x 0.120 x 0.100 mm^3	

Theta range for data collection	1.723 to 24.148°
Index ranges	-16<=h<=16, -14<=k<=14, -17<=l<=15
Reflections collected	16455
Independent reflections	4134 [R(int) = 0.0300]
Completeness to theta = 24.148	99.2 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4134 / 0 / 361
Goodness-of-fit on F^2	1.059
Final R indices [I>2sigma(I)]	R1 = 0.0471, wR2 = 0.1300
R indices (all data)	R1 = 0.0691, wR2 = 0.1578
Extinction coefficient	n/a
Largest diff. peak and hole	0.189 and -0.193 e. $Å^{-3}$

Table S2 Major electronic excitations for **TPE-NBD**, **and DPP-NBD**.

Compound	Excited state	λ/nm [eV]	Osc. str (ƒ)	Major contributions
TPE-NBD	$S_0 \rightarrow S_2$	421.44 [2.94]	0.1405	HOMO-1→LUMO (68%)
	$S_0 \rightarrow S_8$	342.63 [3.61]	0.3966	HOMO→LUMO+2 (69%)
	$S_0 \rightarrow S_1$	566.24 [2.19]	0.0002	HOMO→LUMO (70%)
DPP-NBD	$S_0 \rightarrow S_3$	430.82 [2.87]	0.2651	HOMO-2→LUMO (68%)
	$S_0 \rightarrow S_{11}$	318.14 [3.89]	0.3246	HOMO-2→LUMO+1 (65%)
	$S_0 \rightarrow S_1$	493.66 [2.51]	0.0002	HOMO→LUMO (70%)

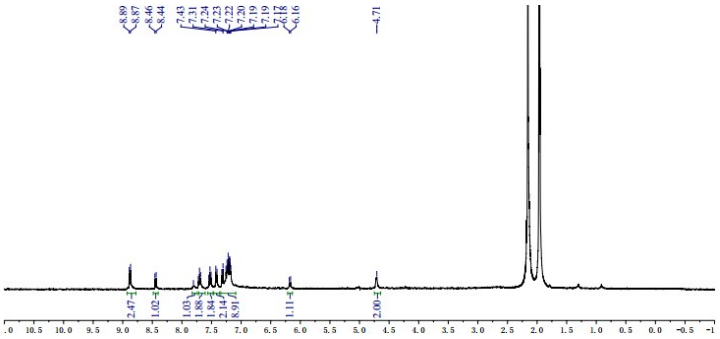


Fig. S9 ^{1}H NMR spectrum of **DPP-NBD**

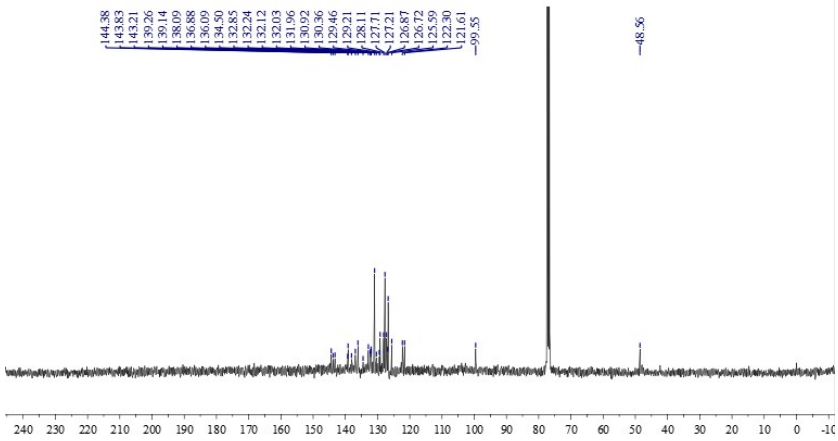


Fig. S10 ^{13}C NMR spectrum of ***DPP-NBD***

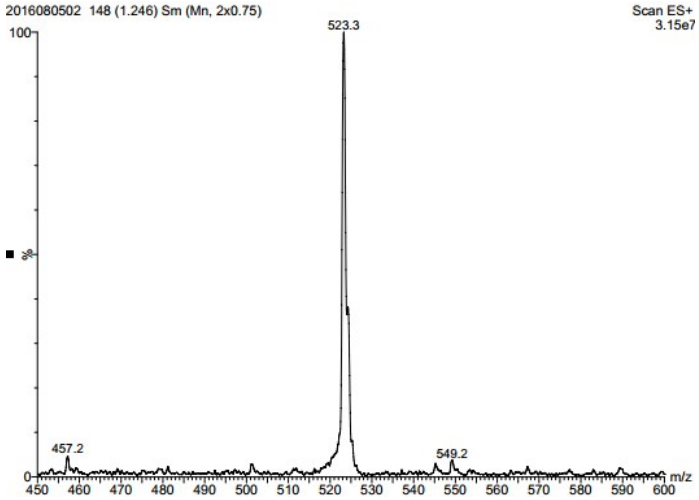


Fig. S11 ESI mass spectrum of **DPP-NBD**

Reference

S1 L. Fabbrizzi, M. Licchelli, A. Poggi, D. Sacchi, C. Zampa *Polyhedron,* 2004, **23**, 373–378.

S2 Sheldrick GM. SHELXS-97, a program for crystal structure solution. Germany: Göttingen; 1997.

S3 Sheldrick GM. SHELXL-97, a program for crystal structure refinement. Germany: Göttingen; 1997.