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Supporting Information

A series of triphenylamine-based two-photon absorbing materials with AIE property for biological imaging

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Synthesis of compound **M1-M3**

Preparation of 4-Nitro-benzyl-triphenylphosphonium bromide (M1)

4-Nitro-benzyl-triphenylphosphonium bromid was prepared referring the literature.[1]

Preparation of 4-Diphenylaminobenzaldehyde (M2)

4-Diphenylaminobenzaldehyde was prepared referring the literature.[2]

Preparation of 4-[N, N'-bis(4-ethoxyphenyl)amino]benzaldehyde (M3)

4-Iodophenetole 233.50 g (1.06 mol) 4-Iodo-phenol and 42.45 g (1.06 mol) NaOH was placed into a dry mortar and well milled into powder, and then the mixture was transfered to 1000 mL round-bottom flask equipped with a magnetic stirrer. 300 mL of bromoethane, 15 mL of N, N-dimethylformamide and a catalytic amount of CsOH were added to the flask. The reactants were stirred at room temperature for 1 h, and then the mixture was heated up gradually to 80 ºC and refluxed for about 70 h. Thin layer chromotography (TLC) confirmed the absence of the starting material for the reactions. The solvent bromoethane was evaporated under reduced pressure after the solution was cooled to room temperature, and firstly appropriate amount of dichloromethane was added with stirring, secondly appropriate amount of water was added, separated and the organic layer solution was obtained, dried by anhydrous $MgSO_4$, filtered and concentrated. 252.43 g red oil was obtained. Yield: 96.2%. ^{1}H-NMR: (400 Hz, $(CD_3)_2SO$), δ (ppm): 7.57 (d, J = 8.8 Hz, 2H), 6.76 (d, J = 8.8 Hz, 2H), 3.98 (q, J = 6.9 Hz, 2H), 1.30 (t, J = 7.0 Hz, 3H). IR (KBr, cm^{-1}): 2979, 2929, 1586, 1486, 1392, 1244, 1047, 820, 630, 507. HRMS (GCT-MS) Calcd for C_8H_9IO, 247.97; Found, 247.9692.

N, N'-bis(4-ethoxyphenyl)phenylamine A suspension of 2.32 g (25 mmol) of Phenylamine, 20.86 g (75 mmol) of 4-Iodophenetole and 200 mL 1, 2-dichlorobenzene were added into a three-necked flask equipped with a magnetic stirrer, a reflux condenser, and a nitrogen input tube, and then 17.94 g (130 mmol) of anhydrous K_2CO_3 and 8.34 g (130 mmol) copper powder were added slowly. At last, a catalytic amount of 18-crown-6 was added under stirred. The reaction mixture was refluxed for 12 h in a heating mantle under nitrogen and monitored by TLC. After completion of the reaction, the solvent 1, 2-dichlorobenzene was evaporated under reduced pressure after the solution was cooled to room temperature.The crude product was purified by column chromatography with petroleum

(b.p. 60-90 ºC)/ethyl acetate (20:1 by volume) to yield 2.2 g of pale yellow oil. Yield: 26.4%. ^{1}H-NMR: (400 Hz, $(CD_3)_2CO$), δ (ppm): 7.18 (t, J = 7.6 Hz, 2H), 7.02 (d, J = 8.4 Hz, 4H), 6.86 (q, J = 8.1 Hz, 7H), 4.04 (q, J = 6.9 Hz, 4H), 1.37 (t, J = 7.0 Hz, 6H). IR (KBr, cm^{-1}): 3034, 2977, 2932, 2893, 2855, 1597, 1507, 1324, 1245, 1162, 827,753, 695.

4-[N, N'-bis(4-ethoxyphenyl)amino]benzaldehyde (M3)

4-[N, N'-bis(4-ethoxyphenyl)amino]benzaldehyde was prepared referring the literature.[29] Yellow oil was obtained. Yield: 40.7%. ^{1}H-NMR: ((400 Hz, $CD_3)_2CO$), δ (ppm): 9.76(s, 1H), 7.67 (d, J = 8.4 Hz, 2H), 7.19 (d, J = 8.8 Hz, 4H), 6.98 (d, J = 8.4 Hz, 4H), 6.78 (d, J = 8.8 Hz, 2H), 4.07 (q, J = 6.9 Hz, 4H), 1.38 (t, J = 7.0 Hz, 6H). IR (KBr, cm^{-1}): 3039, 2974, 2927, 2870, 1690, 1592, 1561, 1505, 1471, 1240, 1161, 826, 717, 684. HRMS (GCT-MS) Calcd for $C_{23}H_{23}NO_3$, 361.17; Found, 361.1653.

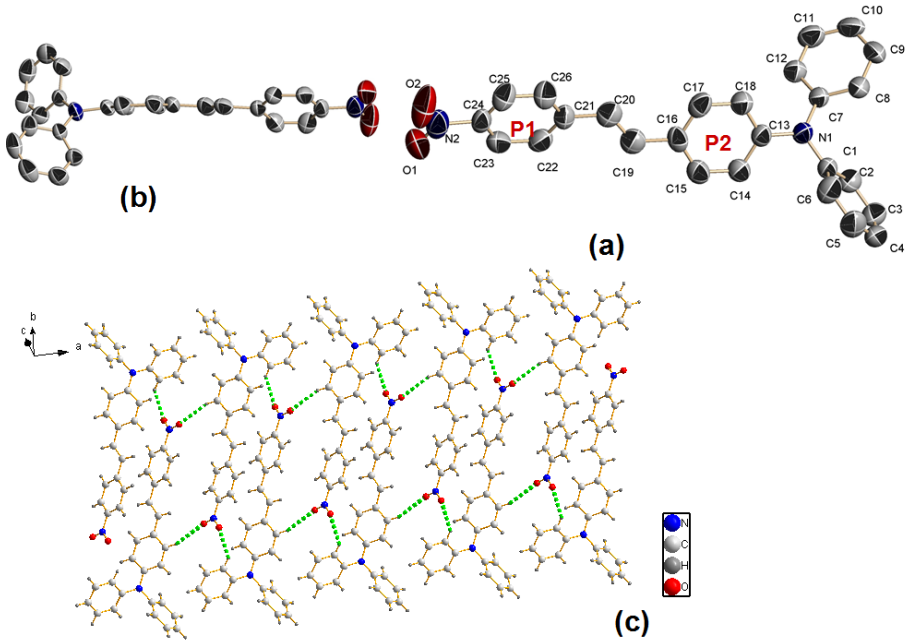

Fig. S1. (a) ORTEP diagram of **1A**, Hydrogen atoms are omitted for clarity. (b) the side elevation of **1A**. (c) One-dimensional chain of **1A** showing the N-O···H (green) along the *a*-axis.

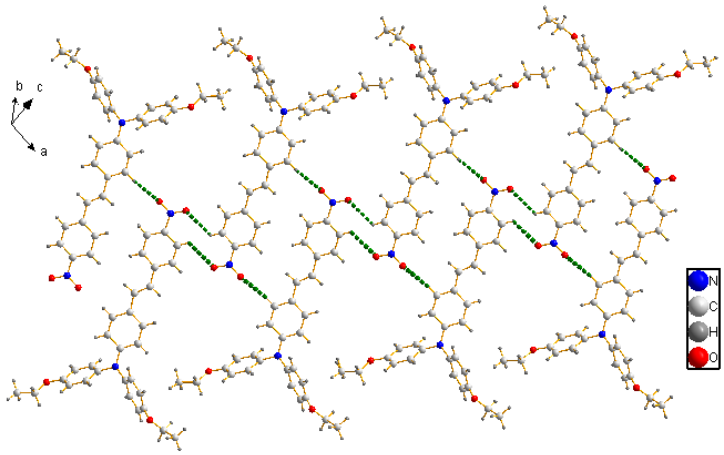

Fig. S2. One-dimensional chain of **2A** showing the C-H···O (green) along the *a*-axis

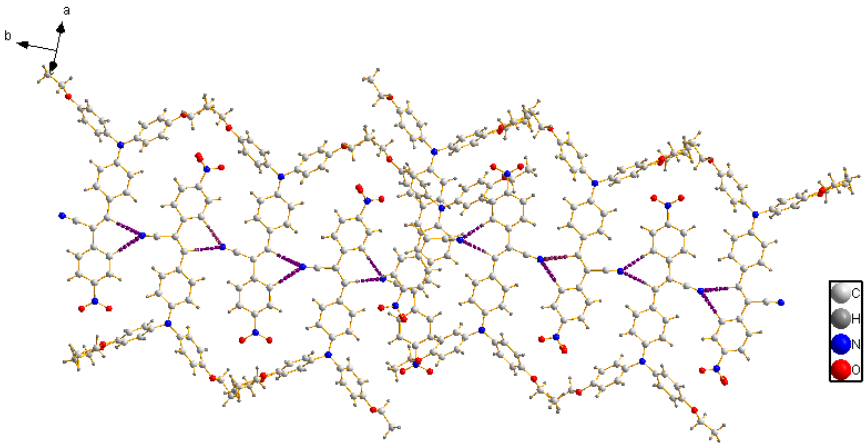

Fig. S3. One-dimensional chain of **3A** showing the C-H···N (violet) along the *b*-axis.

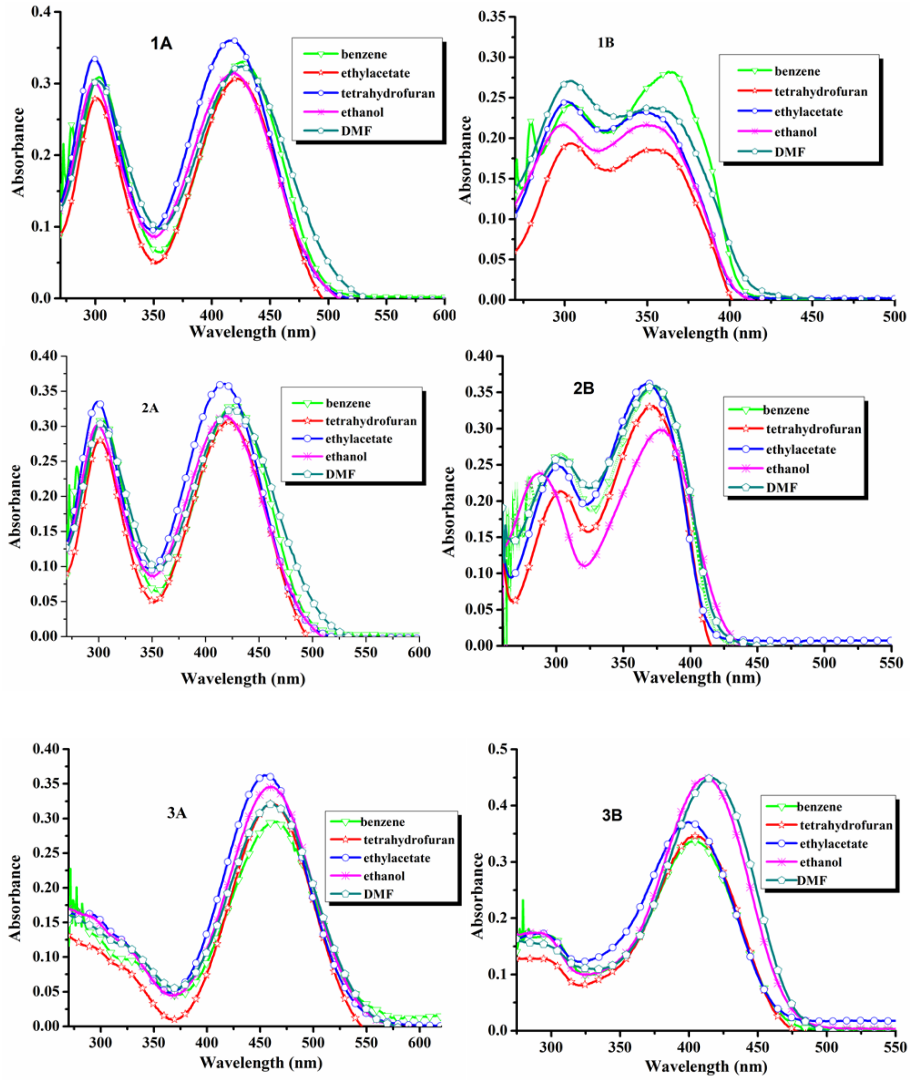

Fig.S4. Linear absorption spectra of chromophores **1A-3A** and **1B-3B** in five organic solvents of different polarities

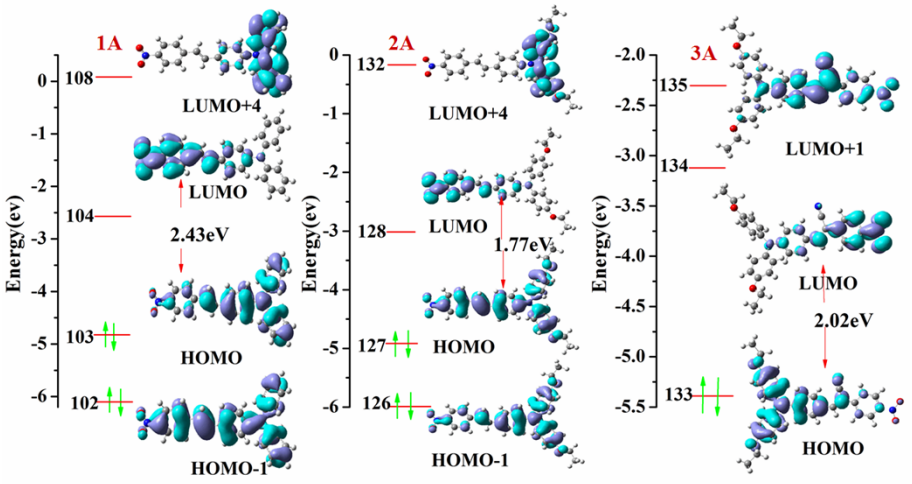

Fig. S5. Molecular orbital energy diagram of **1A-3A**

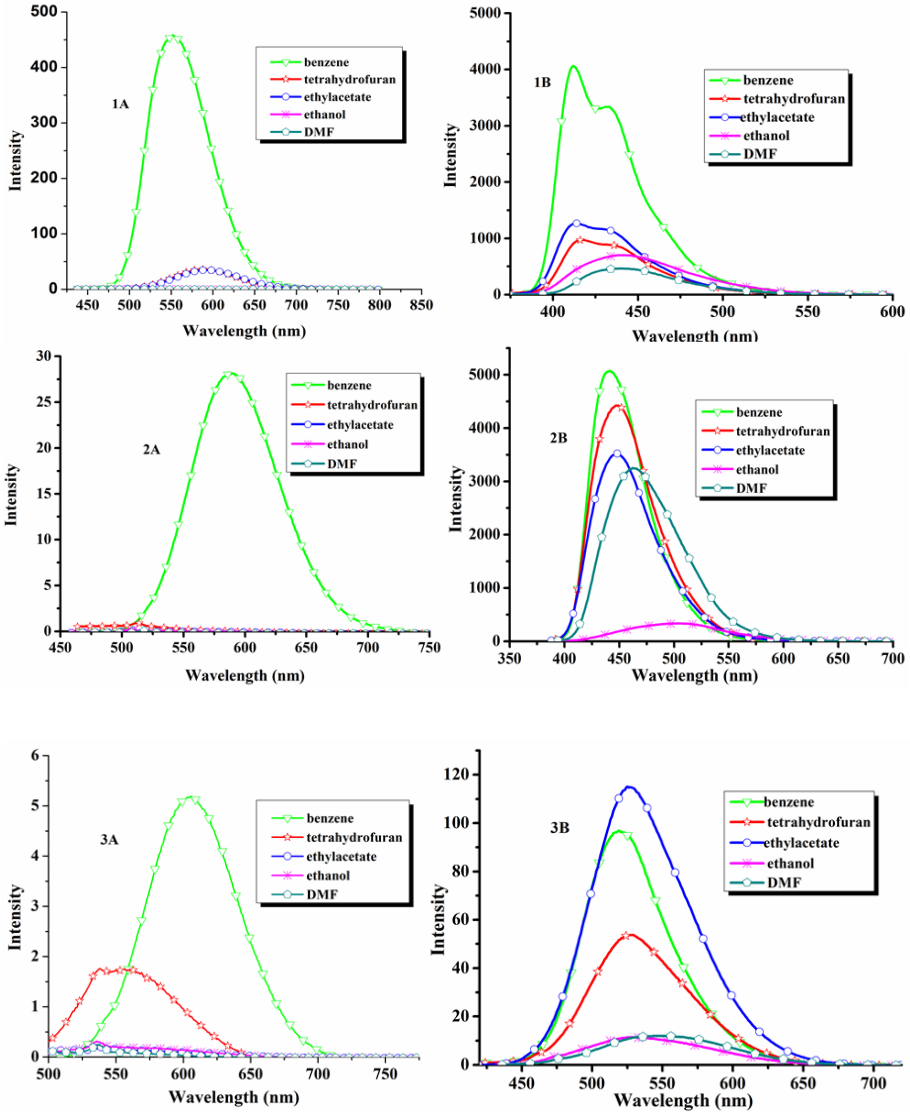

Fig. S6. One-photon fluorescence spectra of chromophores **1A-3A** and **1B-3B** in five organic solvents of different polarities

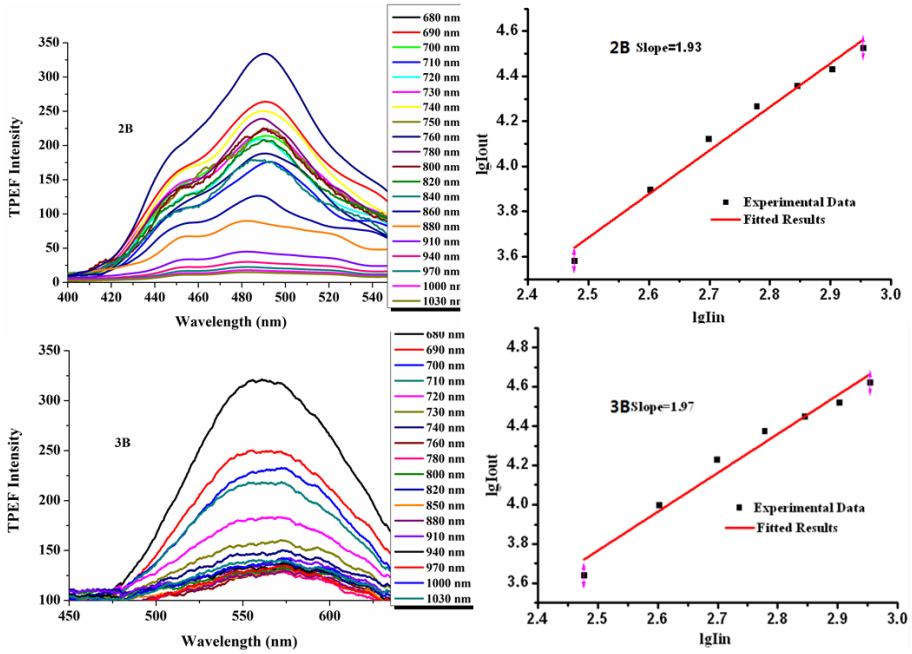

Fig. S7. (left) The TPEF spectra of chromophores **2B** and **3B** in ethyl acetate pumped by femtosecond laser at 300 mw under different excitation wavelengths. (right) The logarithmic plots of the fluorescence integral of chromophores versus different excitation intensities at 700 nm

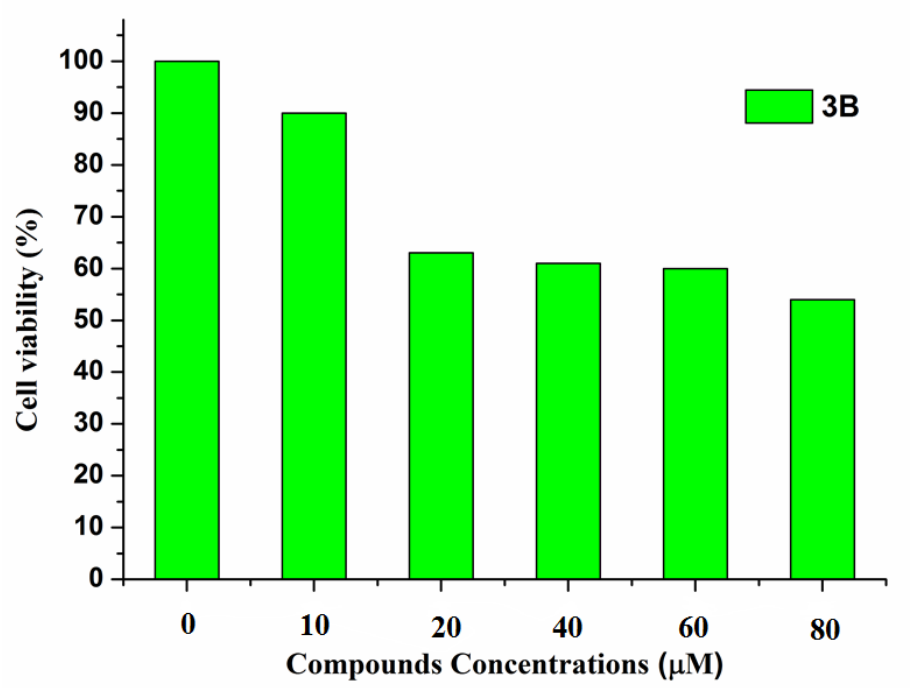

Fig. S8. Cytotoxicity data results obtained from the MTT assay ($c = 1 \times 10^{-4}$ M)

Table S1 Crystal data collection and structure refinement of **1A-3A** and **3B**

Compd	**1A**	**2A**	**3A**	**3B**
Chemical Formula	$C_{26}H_{20}N_2O_2$	$C_{30}H_{28}N_2O_4$	$C_{62}H_{54}N_6O_8$	$C_{31}H_{29}N_3O_2$
Formula weight	392.44	480.54	1011.11	475.57
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/c$	$P2_1$	$P\bar{1}$	$P2_1$
a(Å)	8.488(5)	10.326(5)	11.899(5)	10.717(5)
b(Å)	8.983(5)	22.629(5)	12.656(5)	13.917(5)
c(Å)	27.088(5)	12.174(5)	18.797(5)	17.565(5)
α (o)	90.000	90.000	85.623(5)	90.000
β (o)	96.500(5)	114.636(5)	74.828(5)	92.417(5)
γ (o)	90.000	90.000	87.564(5)	90.000
V(Å3)	2052.1(2)	2585.7(2)	2723.3(2)	2617.5(2)
Z	4	4	2	4
R_1, wR_2 [$I \geq 2\sigma(I)$]	0.0574, 0.1511	0.0688, 0.1895	0.0764, 0.2228	0.0506, 0.1390
R_1, wR_2 *[all data]*	0.0973, 0.1833	0.1583, 0.2322	0.1274, 0.2640	0.1023, 0.1797
Goodess-of-fit on F2	1.026	0.994	1.044	1.005

Table S2. Selected bond lengths [Å] and angles [°] for **1A-3A** and **3B**

			1A		
C(21)-C(20)	1.491(4)	C(19)-C(16)	1.484(4)	C(19)-C(20)	1.266(4)
C(7)-N(1)-C(1)	119.2(2)	C(13)-N(1)-C(7)	120.8(2)	C(1)-N(1)-C(13)	119.6(2)
			2A		
C(22)-C(23)	1.498(6)	C(21)-C(20)	1.465(5)	C(22)-C(21)	1.280(5)
N(1)-O(3)	1.216(5)	N(1)-O(4)	1.211(6)	C(3)-O(1)	1.456(2)
C(15)-N(2)-C(9)	119.5(3)	C(15)-N(2)-C(6)	120.6(3)	C(9)-N(2)-C(6)	117.2(3)
O(4)-N(1)-O(3)	123.2(5)	C(22)-C(21)-C(20)	127.4(4)	O(3)-N(1)-C(28)	119.2(6)
			3A		
C(10)-C(9)	1.452(5)	C(9)-C(7)	1.354(5)	C(7)-C(4)	1.487(4)
C(7)-C(8)	1.443(5)	C(8)-N(3)	1.136(4)	C(19)-O(3)	1.366(5)
C(16)-N(2)-C(13)	123.1(3)	C(24)-N(2)-C(13)	120.0(3)	C(16)-N(2)-C(24)	116.9(3)
C(7)-C(8)-N(3)	176.5(4)	C(10)-C(9)-C(7)	133.5(3)	O(1)-N(1)-O(2)	107.9(2)
			3B		
C(26)-C(24)	1.481(3)	C(24)-C(23)	1.348(3)	C(23)-C(20)	1.457(3)
C(24)-C(25)	1.436(4)	C(25)-N(1)	1.154(3)	N(2)-H(2A)	0.860(2)
C(24)-C(25)-N(1)	177.5(3)	C(26)-C(24)-C(23)	126.2(2)	C(4)-N(3)-C(17)	120.9(2)
C(8)-N(3)-C(17)	120.7(2)	C(8)-N(3)-C(4)	118.3(2)	H(2A)-N(2)-C(29)	120.0

Table S3. Photophysical properties of dyes **1A- 3A** and **1B-3B** in five different solvents

Compd	Solvents	λmax^{a}(Ɛmax^{b})	λmax^{c}	Φ	τ/ns	Δv(cm^{-1})	λmax^{d}	σ/GM	$\sigma\times\Phi$
	benzene	302(2.4), 363(2.8)	529	0.140	1.02	3125			
	THF	302(1.9), 352(3.2)	548	0.051	0.47	4246			
1B	ethyl acetate	301(2.5), 347(2.3)	414	0.050	0.51	4664			
	ethanol	299(2.2), 350(2.2)	439	0.037	0.38	5792			
	DMF	303(2.7), 353(2.4)	440	0.022	0.35	5601			
	benzene	303(2.7), 372(3.3)	441	0.160	1.61	4206			
	THF	303(2.1), 372(3.3)	447	0.150	0.73	4510			
2B	ethyl acetate	301(2.5), 368(3.6)	448	0.104	0.73	4852	500	3160	527
	ethanol	287(2.4), 377(3.0)	508	0.018	0.49	6840			
	DMF	303(2.6), 374(3.6)	463	0.123	1.73	5140			
	benzene	405(3.4)	519	0.0039	0.45	5424			
	THF	404(3.5)	525	0.0021	1.31	5705			
3B	ethyl acetate	399(3.7)	527	0.0042	0.97	6087	550	98369	394
	ethanol	413(4.5)	528	0.0004	0.04	5274			
	DMF	416(4.5)	546	0.0004	0.05	5723			
	benzene	303(3.1), 426(3.3)	550						
	THF	301(2.8), 418(3.6)	587						
1A	ethyl	299(3.0), 418(3.6)	591						
	ethanol	299(3.0), 418(3.2)							
	DMF	302(3.0), 352(3.2)							
	benzene	304(2.2), 446(2.7)	587						
	THF	303(2.2), 444(2.7)							
2A	ethyl acetate	301(2.4), 439(3.0)							
	ethanol	300(2.3), 440(2.6)							
	DMF	303(2.6), 374(3.6)							
	benzene	463(3.0)							
	THF	459(3.2)							
3A	ethyl acetate	454(3.6)	518						
	ethanol	460(3.4)	527						
	DMF	461(3.2)	528						

a: Absorption peak position in nm, b: Maximum molar absorbance in 10^4 mol^{-1} L cm^{-1} , c: Peak position of OPEF spectra in nm. Φ: Fluorescence quantum yield, τ: Fluorescence lifetime, Δv: Stokes shift in cm^{-1}, e: The TPEF peak position in nm. σ: 2PA cross section in GM, $\sigma\times\Phi$: two-photon action cross-section.

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3.1 molecular quadratic hyperpolarizabilities of ene-, imine-, and azo-linked

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