Supplementary Information

Highly efficient dual-state emission and two-photon absorption of novel naphthalimide functionalized cyanostilbene derivatives with finely tuned terminal alkoxyl groups

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Materials and instruments

All the chemicals and solvents were purchased from the commercial suppliers without further purification. The solvents used for UV-vis absorption and fluorescence measurements were in analytical grade. ¹H NMR (400 MHz) and ¹³C NMR (100 MHz) spectra were recorded on a Bruker Avance 400 MHz spectrometer, using CDCl₃ as the solvent and tetramethylsilane (TMS) as the internal standard. The triple quadrupole mass spectra were measured with an atmospheric chemical ionization (APCI) equipment with Mass Hunter software. UV-vis absorption spectra were recorded using a TU-1901 spectrometer from Beijing Purkinje General Instrument Co., Ltd with samples in solution or in a quartz cuvette (path length 1 cm). Fluorescence spectra were obtained on a Hitachi FL-7000 (Hitachi high technologies corporation Tokyo Japan). The powder X-ray diffraction (PXRD) patterns were recorded on an MXP18AHF diffractometer using CuKa radiation ($\lambda = 1.54$ Å) in the 2 θ range from 5° to 50°. The absolute photoluminescence quantum yield in the solid state was measured on a HORIBA FluoroMax-4P spectrofluorometer using an integrating sphere (HORIBA Scientific, F-3092 integrating sphere). The time-correlated single photon counting (TCSPC) experiments were performed on a Horiba Fluoro max plus. The single-crystal X-ray diffraction measurements were performed on a STOE STADIVARI X-ray diffractometer using graphite-monochromated CuKa radiation. The theoretical calculation was carried out with Gaussian 09 program package at B3LYP/6-311G** level with empirical dispersion correction considered.¹

The 2PA measurement was carried out with a femtosecond laser pulse, and a Ti: sapphire system (680-1080 nm, 80 MHz, 140 fs, Coherent Astrella) was used as the light source. The 2PEF was analyzed by an Ocean Optics QE65 Pro spectrometer. For solution measurements the samples were prepared in a 1 cm quartz cuvettes. The 2PA cross sections are calculated based on the following equation:

$$\delta_s = \frac{C_r \cdot n_s \cdot F_s \cdot Q_r}{C_s \cdot n_r \cdot F_r \cdot Q_s} \, \delta_r$$

where *C* is the solution concentration, *n* is the refractive index, *F* is the fluorescence intensity, *Q* is the quantum yield, in which the subscript character *r* and *s* indicate that the values are corresponding to the reference and the sample, respectively. The δ_r at each wavelength are derived

from literature.² For the aggregated state measurement the samples were prepared in a 1 mm quartz cuvettes. The 2PA cross sections are calculated based on the same equation, for details refer to the literature.³

Synthesis of compounds

Compound 3

In a 100 mL round-bottom flask, **1** (2.00 g, 6.02 mmol) and **2** (1.35 g, 9.03 mmol) were added. The system was degassed with N₂, then Pd(PPh₃)₄ (0.01 g, 0.08 mmol), K₂CO₃ solution (2 M in H₂O, 10 mL), THF (30 mL) were added successively. The mixture was refluxed for 10 h, and then cooled down to room temperature. The resulted solution was extracted by CH₂Cl₂ (3 × 50 mL), and the organic layer was separated, followed by drying with anhydrous Na₂SO₄. The solvents were evaporated to get the crude product, which was further purified by column chromatography (petroleum ether : CH₂Cl₂ = 1 : 3, v/v). The target compound was obtained as light yellow powder (1.57 g, 4.39 mmol), yield 73% ¹H NMR (400 MHz, CDCl₃, ppm) δ : 0.98 (t, 3H, *J* = 7.40 Hz), 1.41-1.50 (m, 2H), 1.69-1.77 (m, 2H), 4.20 (t, 2H, *J* = 7.52 Hz), 7.67-7.73 (m, 4H), 8.06 (d, 2H, *J* = 8.4 Hz), 8.16 (d, 1H, *J* = 8.52 Hz), 8.63-8.66 (m, 2H), 10.14 (s, 1H) ¹³C NMR (100 MHz, CDCl₃, ppm) δ : 191.74, 164.22, 164.01, 145.17, 145.04, 136.23, 131.97, 131.44, 130.72, 130.05, 129.78, 128.73, 127.93, 127.38, 123.20, 122.72, 40.43, 30.30, 20.48, 13.94.

Compound NICS-M

In a 250 mL round-bottom flask, **3** (0.50 g, 1.40 mmol), **5-R** (R = methyl, 0.24 g, 1.68 mmol), and ethanol (80 mL) were added successively. The mixture was refluxed until all the solids were fully dissolved, then *t*-BuOK (0.31 g, 2.80 mmol) was added. The system was further refluxed for another 1 h, then the solution was filtrated to give the crude product, which was purified by column chromatography (petroleum ether : CH₂Cl₂ = 1 : 3, v/v) as light green powder, yield 95%. ¹H NMR (400 MHz, CDCl₃, ppm) δ : 0.98 (t, 3H, *J* = 7.40 Hz), 1.41-1.51 (m, 2H), 1.70-1.78 (m, 2H), 3.87 (s, 3H), 4.21 (t, 2H, *J* = 7.60 Hz), 6.98 (d, 2H, *J* = 8.80 Hz), 7.52 (s, 1H), 7.60 (d, 2H, *J* = 8.20 Hz), 7.66 (d, 2H, *J* = 8.84 Hz), 7.70-7.74 (m, 2H), 8.03 (d, 2H, *J* = 8.24 Hz), 8.26 (d, 1H, *J* = 8.48 Hz), 8.63-8.66 (m, 2H). ¹³C NMR (100 MHz, CDCl₃, ppm) δ : 163.29, 163.08, 159.77, 144.72, 139.52, 137.95, 133.25, 131.31, 130.34, 129.79, 129.50, 128.89, 128.35, 127.76, 126.49, 126.15, 125.74, 122.09, 121.26, 117.11, 113.60, 111.37, 54.54, 39.36, 29.28, 19.45, 12.91. APCI-MS: m/z calcd: 486.1943, found = 486.1924.

Compound NICS-E

NICS-E was prepared with a similar procedure with that of **NICS-M**, light green powder, yield 93%. ¹H **NMR** (400 MHz, CDCl₃, ppm) δ : 0.98 (t, 3H, J = 7.40 Hz), 1.41-1.49 (m, 5H), 1.70-1.77 (m, 2H), 4.09 (dd, 2H, $J_1 = 7.00$, $J_2 = 14.00$), 4.21 (d, 2H, J = 7.64 Hz), 6.97 (d, 2H, J = 15.12 Hz), 7.52 (s, 1H), 7.59 (d, 2H, J = 8.32 Hz), 7.64 (d, 2H, J = 8.92 Hz), 7.70-7.74 (m, 2H), 8.02 (d, 2H, J = 8.16 Hz), 8.26 (d, 2H, J = 8.52 Hz), 8.62-8.66 (m, 2H). ¹³C **NMR** (100 MHz, CDCl₃, ppm) δ : 164.35, 164.14, 160.21, 145.79, 140.53, 138.85, 134.33, 132.36, 131.39, 130.84, 130.54, 129.95, 129.38, 128.81, 127.91, 127.52, 127.19, 126.59, 123.14, 122.30, 118.18, 115.13, 112.48, 63.83, 40.40, 30.32, 20.49, 14.83, 13.95. **APCI-MS**: m/z found: 500.2100, found = 500.2066.

Compound NICS-P

NICS-P was prepared with a similar procedure with that of **NICS-M**, light green powder, yield 92%. ¹H **NMR** (400 MHz, CDCl₃, ppm) δ : 0.98 (t, 3H, J = 7.36 Hz), 1.05 (t, 3H, J = 7.40 Hz), 1.41-1.51 (m, 2H), 1.70-1.77 (m, 2H), 1.79-1.88 (m, 2H), 3.97 (t, 2H, J = 6.56), 4.20 (t, 2H, J = 7.48 Hz), 6.67 (d, 2H, J = 8.76 Hz), 7.51 (s, 1H), 7.59 (d, 2H, J = 8.12 Hz), 7.64 (d, 2H, J = 8.72 Hz), 7.69-7.72 (m, 2H), 8.03 (d, 2H, J = 8.20 Hz), 8.26 (d, 1H, J = 8.52 Hz), 8.62-8.66 (m, 2H). ¹³C **NMR** (100 MHz, CDCl₃, ppm) δ : 163.29, 163.09, 159.38, 144.74, 139.47, 137.76, 133.30, 131.32, 130.34, 129.79, 129.50, 128.89, 128.34, 127.76, 126.87, 126.45, 126.15, 125.49, 122.10, 121.25, 117.14, 114.12, 111.44, 68.81, 39.36, 29.28, 21.57, 19.46, 12.92, 9.55. **APCI-MS**: m/z calcd: 514.2256, found = 514.2237.

Compound NICS-B

NICS-B was prepared with a similar procedure with that of NICS-M, light green powder, yield 91%. ¹H NMR (400 MHz, CDCl₃, ppm) δ: 0.96-1.00 (m, 6H), 1.41-1.56 (m, 4H), 1.70-1.83 (m, 4H), 3,87 (s, 3H), 4.01 (t, 2H, *J* = 6.48 Hz), 4.20 (t, 2H, *J* = 7.60 Hz), 6.96 (d, 2H, *J* = 8.80 Hz), 7.51 (s, 1H), 7.59 (d, 2H, *J* = 8.16 Hz), 7.63 (d, 2H, *J* = 8.76 Hz), 7.69-7.73 (m, 2H), 8.02 (d, 2H, *J* = 8.20 Hz), 8.26 (d, 1H, *J* = 8.44 Hz), 8.62-8.65 (m, 2H). ¹³C NMR (100 MHz, CDCl₃, ppm) δ: 159.39, 144.75, 139.47, 137.75, 133.30, 131.32, 130.34, 129.80, 129.50, 128.90, 128.34, 127.77, 126.87, 126.45, 126.15, 125.48, 122.10, 121.26, 117.14, 114.11, 111.45, 67.02, 39.36, 30.27, 29.28, 19.46, 18.28, 12.90. APCI-MS: m/z calcd: 528.2413, found = 528.2412.

Figures and tables

Table S1. Summary of crystallographic data and structure refinement details for NICS-X (X = M, E, P, B, respectively).

Identification code	NICS-M	NICS-E	NICS-P	NICS-B
Formula	$C_{32}H_{26}N_2O_3$	$C_{33}H_{28}N_2O_3$	$C_{34}H_{30}N_2O_3$	$C_{35}H_{32}N_2O_3$
Formula weight	486.55	500.57	514.60	528.62
Temperature (K)	293	293	120	295
Wavelength (Å)	1.54186	1.54186	1.54186	1.54186
Crystal system	triclinic	triclinic	triclinic	triclinic
Space group	$P\overline{1}$	$P\overline{1}$	$P\overline{1}$	$P\overline{1}$
<i>a</i> (Å)	6.9932(4)	4.8452(3)	6.9068(4)	6.9359(5)
<i>b</i> (Å)	10.2229(6)	11.0143(7)	14.1157(8)	14.6572(10)
<i>c</i> (Å)	17.2620(10)	23.5028(14)	14.6968(8)	15.3464(11)
α (°)	91.517(4)	92.933(5)	69.523(4)	65.562(5)
β (°)	98.755(4)	90.978(5)	83.612(4)	83.624(5)
γ (°)	95.809(4)	97.974(5)	88.274(5)	86.870(5)
Volume	1212.33(12)	1240.11(13)	1333.92(13)	1411.51(18)
Z	2	2	2	2
$D_{\text{caled}} [\text{g/cm}^3]$	1.3329	1.3406	1.2812	1.2438
Absorption coefficient (mm ⁻¹)	0.685	0.684	0.650	0.627
F (000)	512.0	528.0	544.0	560.0
_reflns_number_gt	3629	3122	3679	3257
_reflns_number_total	4336	4421	4467	4545
Coodness-of-fit on F^2	1.053	1.009	1.095	1.020
Final <i>R</i>	$R_1 = 0.057\overline{6}$	$R_1 = 0.0463$	$R_1 = 0.0776$	$R_1 = 0.0641$
[<i>I</i> > 2 σ (<i>I</i>)]	$wR_2 = 0.1300$	$wR_2 = 0.1505$	$wR_2 = 0.2306$	$wR_2 = 0.2150$

Table S2. Summarized shifts of the most pronounced absorption and PL peaks in different solvents (CHe = Cyclohexane, Tol = Toluene, DOX = 1,4-Dioxane, ChF =Chloroform, EA = Ethyl acetate, THF = Tetrahydrofuran, DCM = Dichloromethane, DMF = N,N-Dimethyl formamide, Ace = Acetone, ACN = Acetonitrile).

Compounds	Solvents	λ_{ab}	λ_{em}	$\Delta\lambda$ (cm ⁻¹)	ε L/(mol·cm)
NICS-M	CHe (-0.0017)	372.78	433.53	3759.01901	4.93×10 ⁴
	Tol (0.0132)	380.83	442.93	3681.50463	4.48×10^{4}
	DOX (0.0245)	378.27	467.56	5048.5141	4.87×10^{4}
	ChF (0.1483)	381.46	467.68	4832.92679	4.78×10^{4}
	EA (0.1996)	375.75	470.93	5378.8614	4.36×10^4
	THF (0.2096)	378.77	477.72	5468.48218	4.39×10^{4}
	DCM (0.2184)	380.68	481.30	5491.72006	4.55×10^{4}
	DMF (0.2744)	383.21	530.54	7246.63225	4.51×10^{4}
	Ace (0.2887)	375.46	503.51	6773.41689	4.58×10^{4}
	ACN (0.3054)	377.43	532.83	7727.26717	4.76×10^{4}
NICS-E	CHe (-0.0017)	374.35	436.16	3785.60304	6.25×10^4
	Tol (0.0132)	381.77	445.18	3730.95757	5.89×10^{4}
	DOX (0.0245)	377.68	448.64	4187.85491	6.17×10^4
	ChF (0.1483)	380.27	473.43	5174.65786	6.06×10^4
	EA (0.1996)	374.44	474.68	5639.72448	5.75×10^{4}
	THF (0.2096)	377.34	480.72	5699.16843	5.56×10^4
	DCM (0.2184)	379.25	485.05	5751.39995	5.63×10^4
	DMF (0.2744)	381.97	533.12	7422.5635	5.73×10^4
	Ace (0.2887)	375.81	509.05	6964.7551	5.74×10^{4}
	ACN (0.3054)	376.59	528.25	7623.64671	5.97×10^4
NICS-P	CHe (-0.0017)	373.87	436.13	3818.32189	5.98×10^4
	Tol (0.0132)	381.66	445.27	3743.04729	5.12×10^4
	DOX (0.0245)	378.01	447.97	4131.4032	5.63×10^4
	ChF (0.1483)	380.66	472.89	5123.59549	5.75×10^4
	EA (0.1996)	374.50	475.26	5661.15536	4.89×10^4
	THF (0.2096)	377.92	481.43	5689.17487	4.21×10^4
	DCM (0.2184)	379.56	486.26	5781.16594	4.80×10^4
	DMF (0.2744)	381.93	533.21	7428.47143	4.87×10^4
	Ace (0.2887)	375.41	508.79	6983.06861	5.64×10^4
	ACN (0.3054)	377.26	528.58	7588.30618	5.20×10 ⁴
NICS-B	CHe (-0.0017)	374.47	435.67	3751.25628	5.54×10^4
	Tol (0.0132)	381.68	445.52	3754.27663	4.99×10 ⁴
	DOX (0.0245)	378.36	448.06	4111.41567	5.19×10 ⁴
	ChF (0.1483)	380.86	473.52	5137.935	4.76×10^4
	EA (0.1996)	374.46	475.47	5673.3009	4.83×10^4
	THF (0.2096)	378.03	481.01	5663.33844	4.76×10^4
	DCM (0.2184)	380.49	486.30	5718.46145	4.78×10^4
	DMF (0.2744)	382.05	532.79	7405.46344	4.82×10^4
	Ace (0.2887)	374.66	508.42	7022.0886	4.88×10^{4}
	ACN (0.3054)	376.99	539.01	7973.37105	5.08×10^{4}



Figure S1. Solvatochromic effect of NICS-M (a, b), NICS-E (c, d), NICS-P (e, f), and NICS-B (g, h) in different solvents.



Figure S2. Lippert-Mataga fitting of the solvatochromic effects of NICS-M (a), NICS-E (b), NICS-P (c), and NICS-B (d).



Figure S3. The photos of the 2PEF in solution (left) and in water suspension (right) of NICS-M (a), NICS-E (b), NICS-P (c), and NICS-B (d).





Figure S6. ¹³C NMR spectrum of **NICS-M**.







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