Metal-Free Carbazole Scaffold Dyes as Potential Nonlinear Optical Phores: Molecular Engineering

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1. Experimental Section Details

Chemicals

Commercially available reagents carbazole, nitroaniline, 2-chloro nitroaniline, 2,4-dinitroaniline, 2-Bromo-nitroaniline, and 2,6-dichloronitroaniline, sodium nitrite, Conc HCl, 1-Bromo pentane and sodium dodecyl benzoyl sulphate (NaDBS) were purchased from Aldrich. Standard air-free conditions maintained throughout the reaction by maintaining the nitrogen atmosphere and vacuum through Schlenk line techniques. Analytical thin-layer chromatography was performed using Kieselgel 60F-254 plates from Merck. Column chromatography was carried out on Merck silica gel (60-120 mesh). The solvents chloroform, acetone, and DCM were dried according to the standard procedure. The precursor 9- pentyl- 9H- carbazole is prepared according to the standard literature procedure.

Characterizations

¹H, ¹C, data performed on a Bruker Ascend TM -500 MHz FT NMR spectrometer at room temperature using CDCl₃ as a solvent. All NMR chemical shifts reported in parts per million; downfield shifts reported as positive values from tetramethylsilane (TMS) as standard at 0.00 ppm. High-resolution mass spectroscopy (HRMS) performed on a Bruker Maxis HRMS mass spectrometer, and the LCMS data recorded on Shimadzu Instrument. Fourier-transform infrared (FTIR) spectra (KBr) were recorded using a JASCO-5300 spectrophotometer. UV-VIS and fluorescence spectra were recorded in a 1 cm path length quartz cell on a Shimadzu UV-vis to near IR 3600 spectrophotometer and a Fluoromax-4, J.Y. Horiba spectrofluorometer, respectively. Electrochemical data were obtained by cyclic voltammetry using a conventional three-electrode cell and an Ametek electrochemical analyzer. The working electrode was a glassy carbon rod, the

auxiliary (counter) electrode was a Pt wire, the reference electrode was Ag/AgCl, and the supporting electrolyte was 0.1 M tetrabutylammonium hexafluorophosphate. Density Functional Theory (DFT) and Time-Dependent DFT (TDDFT) calculations were performed using the Gaussian09 program package. The closed-shell configurations of all the Dyes, with neutral were fully S2 optimized in the gas phase. Becke's LYP (B3LYP) exchange-correlation functional with Hay and Wadt's double zeta quality Los Alamos electron effective core potential basis set 6-311 g (d, p) was adopted on all atoms. The minimized geometries were analyzed by vibrational frequencies, resulting in no imaginary frequencies. Thus, the optimized structures correspond to real minima on the potential energy surface. At the optimized geometry, TD-DFT calculations were performed at B3LYP/6-311g (d, p) level of theory in dichloromethane (DCM) solvent employing the Polarizable Continuum Model (PCM), as implemented in Gaussian 09.50 singletsinglet excitations at S₀optimized geometry are calculated. The software GaussSum 2.2.5 was used to simulate the major portion of the absorption spectrum and to interpret the nature of transitions. The molecular orbital surfaces are visualized with Gaussview and the percentage contributions of the HTMs molecular orbitals were calculated using GaussSum. C, H, N data were recorded on the Elementary (Variomicrotube) instrument.

Electrode preparation for EIS

Organic molecules (10 mg/ml) dissolve in a polar organic solvent (chloroform) with/without doping of LIFSI (17uL) and TBAHFP (28 uL), the resultant solution was deposited on a glass substrate via spin coating process and dried at 70°C for 5 min. Then, organic molecules coated (0.36 cm² area) glass substrates were used for EIS analysis at different bias voltage and two-probe electrical property.

1. Synthesis procedure of dyes

Different precursors (nitroaniline, 2-chloro nitroaniline, 2,4-dinitroaniline, 2-Bromonitroaniline, and 2,6-dichloronitroaniine) (1mmol) were dissolved in a conc. HCl. The mixture was cooled with an ice bath to lower than 4°C, and then an aqueous solution containing sodium nitrite (1.2 mmol) was slowly added. The mixture was stirred in the ice bath for 30 min. While the mixture was kept in the ice bath, NaDBS and a solution of 9- pentyl- 9H-carbazole (1 mmol) in dichloromethane were successively added. The resultant mixture was stirred vigorously at room temperature for 24 h. Ethanol was added, and the mixture was heated to remove the dichloromethane layer. The isolated red precipitate was filtered, washed with water, and air-dried. The solid was separated and purified via column chromatography using Hexane: DCM (70|30) as eluent.

2. Characterization of Dyes

DC-CICI

Yield: 60%. ¹H NMR (300 MHz, CDCl₃) δ H 8.68(1H,s), 8.22(2H, s), 8.11-8.07(2H,m), 7.47-7.38(3H,m), 7.28-7.23(1H,q), 4.31-4.26(2H,t,J=6), 1.87-1.82(2H,m), 1.31-1.29(4H,m),0.84-0.82(3H,J=6,t).¹³CNMR(75MHz,CDCl₃)(δ):153.94,146.05,145.72,143.74,141.48,128.08,126.96, 124.41,123.50,121.08,120.52,118.80,109.69,109.28,43.64,29.50,28.84,22.60,14.08.IR(KBr): nu(tilde) (cm–1): 2960, 2914, 2844, 1584, 1521, 1336,1118, 1105, 858, 805, 742,726, 687,617. HRMS: m/z Calcd: for C₂₃H₂₀C₁₂N4O₂ [M]+ 454.10; found: [M+H]⁺ 455.10. LCMS: m/z Calcd: for C₂₃H₂₀C₁₂N4O₂ [M]+ 454.10; found: [M+H]⁺ 455.10. LCMS: m/z Calcd: for C₂₃H₂₀C₁₂N4O₂ [M]+ 454.10; found: [M+H]⁺ 455.10. LCMS: m/z Calcd: for C₂₃H₂₀C₁₂N4O₂ [M]+ 454.10; found: [M+H]⁺ 455.10. LCMS: m/z Calcd: for C₂₃H₂₀C₁₂N4O₂ [M]+ 454.10; found: [M+H]⁺ 455.10. LCMS: m/z Calcd: for C₂₃H₂₀C₁₂N4O₂ [M]+ 454.10; found: [M+H]⁺ 455.10. LCMS: m/z Calcd: for C₂₃H₂₀C₁₂N4O₂ [M]+ 454.10; found: [M+H]⁺ 455.10. LCMS: m/z Calcd: for C₂₃H₂₀C₁₂N4O₂ [M]+ 454.10; found: [M+H]⁺ 455.10. LCMS: m/z Calcd: for C₂₃H₂₀C₁₂N4O₂ [M]+ 454.10; found: [M+H]⁺ 455.10. LCMS: m/z Calcd: for C₂₃H₂₀C₁₂N4O₂ [M]+ 454.10; found: [M+H]⁺ 455.10. LCMS: m/z Calcd: for C₂₃H₂₀C₁₂N4O₂ [M]+ 454.10; found: [M+H]⁺ 455.10. LCMS: m/z Calcd: for C₂₃H₂₀C₁₂N4O₂ [M]+ 454.10; found: [M+H]⁺ 455.10. LCMS: m/z Calcd: for C₂₃H₂₀C₁₂N4O₂ [M]+ 454.10; found: [M+H]⁺ 455.10. LCMS: m/z Calcd: for C₂₃H₂₀C₁₂N4O₂ [M]+ 454.10; found: [M+H]⁺ 455.10. LCMS: m/z Calcd: for C₂₃H₂₀C₁₂N4O₂ 455.34; found 455. Elemental analysis calcd (%) for C₂₃H₂₀C₁₂N₄O₂: C 60.67, H 4.43, N 12.30; found C 60.52, H 4.48, N 12.23.



Figure S1: H NMR of Dye DC-ClCl



Figure S2: C¹³NMR of Dye DC-ClCl



Figure S3: LCMS of Dye DC-ClCl



Figure S4: Elemental analysis of Dye DC-ClCl



Figure S5: HRMS data of Dye DC-ClCl

DC-Cl

Yield: 67%. ¹H NMR (500 MHz, CDCl₃) δ_{II} 8.78-8.77 (1H, d,J=5), 8.32 (1H, s) 8.206-8.17 (4H, m), 7.56-7.48 (3H, m), 7.36-7.33 (1H, m), 4.40-4.37 (3H, J=7.5,t), 1.97-1.91 (2H,m), 1.42-1.39 (4H, m), 0.93-0.90 (3H, J=7.5,t). ¹³C NMR (75 MHz, CDCl₃) (δ): 153.82, 145.96, 145.71, 145.63, 143.61, 141.37, 127.96, 126.81, 124.28, 124.18, 123.45, 123.39, 120.94, 120.38, 118.61, 118.08, 109.54, 109.13, 43.51, 29.68, 28.69, 22.43, 13.89. IR (KBr): nu(tilde) (cm⁻¹): 2956, 2918, 2860, 1593, 1518, 1427, 1332, 1240, 1104, 1033, 901, 805, 743, 607. HRMS: m/z Calcd: for C23H21CIN4O2 [M]+ 420.14; found: [M+H]+ 421.14. LCMS: m/z Calcd: for C23H21CIN4O2 420.89; found 422. Elemental analysis calcd (%) for C23H21CIN4O2: C 65.63, H 5.03, N 13.31 found C 65.49, H 5.08, N 13.23.



Figure S6: H NMR of Dye DC-Cl



Figure S7: C¹³NMR of Dye DC-Cl



Figure S8: LCMS of Dye DC-Cl



Figure S9: Elemental analysis of Dye DC-Cl



Figure S10: Elemental analysis of Dye DC-Cl

Yield: 63%. ¹H NMR (500 MHz, CDCl₃) $\delta_{\rm H}$ 8.78-8.78 (1H, s), 8.42-8.40 (2H, d,J=10), 8.22-8.18 (2H, m), 8.08-8.06 (2H, d,J=10), 7.57-7.48 (3H, m), 7.36-7.33 (1H, m), 4.39-4.36 (2H, J=7,t), 1.98-1.90 (2H, m), 1.45-1.41 (4H, m), 0.93-0.90 (3H, J=7,t). ¹³C NMR (75 MHz, CDCl₃) (δ): 153.67, 145.87, 147.99, 146.26, 143.13, 141.32, 126.65, 124.76, 123.50, 123.00, 121.27, 120.87, 120.18, 118.08, 109.47, 109.10, 43.49, 29.70, 28.72, 22.45, 13.93. IR(KBr): nu(tilde) (cm⁻¹): 3428, 3349, 2918, 2860, 1619, 1512, 1490, 1479, 1324, 1313, 1224, 1142, 1116, 1090, 893, 809, 775, 767, 749, 740. HRMS: m/z Calcd: for C₂₃H21N4O2 [M]⁺ 386.18; found [M+H]⁺ 387.18. LCMS: m/z Calcd. for C₂₃H₂₁N₄O₂ 386.45; found 387. Elemental analysis calcd (%) for C₂₃H₂₁ClN₄O₂: C 71.48, H 5.74, N 14.50 found C 71.32, H 5.68, N 14.41.



Figure S11: H NMR of Dye DC



Figure S12: C¹³NMR of Dye DC



Figure S13: LCMS data of Dye DC



Figure S14: Elemental analysis data of Dye DC



Figure S15: HRMS data of Dye DC

Yield: 60%. ¹H NMR (300 MHz, CDCl₃)δ_H8.78 (1H, s), 8.44 (1H, s), 8.22-8.18 (3H, q), 7.87-7.84 (1H, dd), 7.47-7.45 (3H, d, J=6), 7.36-7.31 (1H, m), 4.38-4.33 (2H, J=9,t), 1.97-1.90(2H, m), (3H, J=9,t). ^{13}C NMR 1.39-1.37 (4H,m), 0.92-0.87 (75 MHz, CDCl₃) (δ): 152.91,147.94,146.85,143.58,141.44,134.70,126.26,123.60,122.81,121.45,121.08,120.50,119.47, 118.47,109.69,109.39,43.65,29.52,28.86,22.60,14.09.IR(KBr): nu(tilde) (cm-1): 2951, 2927, 2856, 1630, 1588, 1535, 1356, 1339, 1259, 1242, 1127, 1090, 1016, 823, 795,765, 742, 726. HRMS: m/z Calcd: for $C_{23}H_{21}N_5O_4$ [M]⁺ 431.16; found [M-H]⁻ 430.24. LCMS: m/z Calcd: for $C_{23}H_{21}N_5O_4$: 431.44; found 432. Elemental analysis calcd (%) for C₂₃H₂₁N₅O₄: C 64.03, H 4.91, N 16.23, O 14.83; found C 64.12, H 4.86, N 16.32.



Figure S16:¹H NMR of Dye DC-NO₂NO₂



Figure S17:¹H NMR of Dye DC-NO₂NO₂



Figure S18: LCMS data of Dye DC-NO₂NO₂



Figure S19: Elemental analysis data of Dye DC-NO₂NO₂



Figure S20: HRMS data of Dye DC-NO₂NO₂

DC-BrNO₂

Yield: 60%. ¹H NMR (500 MHz, CDCl₃) δ_{11} 8.71 (1H, s), 8.21-8.19 (1H, d,J=10), 8.13-8.11 (1H, dd), 8.053-8.049 (1H, d, J=2), 7.81-7.79 (1H, dd), 7.74-7.72 (1H, d, J=10), 7.56-7.53 (1H, J=7.5,t), 7.480-7.475 (2H, d, J=2.5), 7.35 (1H,s), 4.37-4.34 (2H, J=7,t), 1.94-1.90 (2H, m), 1.41-1.38 (4H, m), 0.92-0.89 (3H, J=7,t). ¹³C NMR (75 MHz, CDCl₃) (δ): 146.25, 144.38, 143.23, 141.28, 135.81, 126.81, 126.60, 123.97, 123.47, 123.36, 122.52, 121.00, 120.92, 120.21, 120.03, 119.11, 109.45, 109.17. IR(KBr): nu(tilde) (cm⁻¹): 2960, 2914, 2860, 1597, 1533, 1516, 1324, 1285, 1120, 1090, 1090, 1044, 899, 807, 741, 732. HRMS: m/z Calcd: for C₂₃H₂₁BrN₄O₂ [M]· 464.08; found [M+H]+ 465.09. LCMS: m/z Calcd: for C₂₃H₂₁BrN₄O₂: 465.34; found 465. Elemental analysis calcd (%) for C₂₃H₂₁BrN₄O₂: C 59.36, H 4.55, Br 17.17, N 12.04, O 6.88; found C 59.42, H 4.49, N 12.08.



Figure S21: H NMR of Dye DC-BrNO₂



Figure S22: C¹³NMR of Dye DC-BrNO₂



Figure S23: LCMS data of Dye DC-BrNO₂



Figure S24: Elemental analysis data of Dye DC-BrNO₂



Figure S25: HRMS data of Dye DC-BrNO₂

4.Computational Details:

DFT and TD-DFT calculations were performed using the *Gaussian09* program package.² The closed-shell configurations of the D1, D2, D3, D4, and D5 with neutral were fully optimized in the gas phase. Becke's LYP (B3LYP) exchange-correlation functional ¹⁴ with Hay and Wadt's double zeta quality Los Alamos electron effective core potential basis set 6-311g (d,p) was adopted on all atoms. The minimized geometries were analyzed by vibrational frequencies, resulting in no imaginary frequencies. Thus, the optimized structures correspond to real minima on the potential energy surface. At the optimized geometry, TD-DFT calculations were performed at B3LYP/6-311g (d,p) level of theory in Dichloromethane (DCM) solvent employing the polarizable continuum model ⁴² (PCM), as implemented in *Gaussian 09.50* singlet-singlet excitation at S₈ optimized geometry are calculated. The software *GaussSum 2.2.5* was used to simulate the major portion of the absorption spectrum and to interpret the nature of transitions. The molecular orbital surfaces are visualized with *GaussVuew* vand the percentage contributions of the HTMs molecular orbitals were using *GaussSum*.



 Table S1 Molecular orbital pictures of DC-CICI calculated at B3LYP/6-311g (d,p) level of theory.



Table S2 Molecular orbital pictures of **DC-Cl** calculated at B3LYP/6-311g (d,p) level of theory.



 Table S3 Molecular orbital pictures of DC calculated at B3LYP/6-311g (d,p) level of theory.

DC-		
NO ₂ N		
O ₂		
НОМО	LUMO	
НОМО	LUMO	
-1	+1	
НОМО	LUMO	
-2	+2	

Table S4 Molecular orbital pictures of **DC-NO₂NO₂**calculated at B3LYP/6-311g (d,p) level of theory.



Table S5 Molecular orbital pictures of **DC-BrNO**₂ calculated at B3LYP/6-311g (d,p) level of theory.

DC-		
CICI		

State	Wavelength	Osc.strength	Major Contribs	Minor Contribs
	(nm)			
S1				H-2->L+1 (33%)
	479.4624	0.1192	H-2->LUMO (42%)	H-5->L+1 (3%)
S2			HOMO->LUMO	HOMO->L+1 (14%)
	391.4631	1.0531	(65%)	H-5->LUMO (2%)
S3				H-8->L+1 (18%)
	348.1724	0.0024	H-8->LUMO (64%)	H-8->L+5 (3%)
S4				H-1->L+1 (25%)
				HOMO->LUMO
	339.7386	0.0061	H-1->LUMO (60%)	(2%)
S5				H-13->LUMO (35%)
	299.8844	0.0012	H-17->LUMO (19%)	H-12->LUMO (15%)
S 6	298.1249	0.0256	H-4->LUMO (86%)	H-2->L+2 (4%)
S 7				H-2->L+1 (14%)
	296.5491	0.0377	H-2->LUMO (27%)	HOMO->L+1 (38%)
S 8			HOMO->LUMO	HOMO->L+1 (19%)
	289.1962	0.2247	(16%)	HOMO->L+3 (32%)
S9				HOMO->L+1 (11%)
	282.7397	0.0567	H-2->LUMO (12%)	HOMO->L+3 (40%)
S10				H-3->LUMO (34%)
	264.669	0.2326	H-5->LUMO (10%)	H-2->L+1 (17%)

Table S6 Experimental λ_{max} , calculated λ_{max} , (nm) and oscillator strengths (f) of **DC-CICI** in DCM solvent, calculated at B3LYP/6-311g (d,p):

DC-Cl				
State	Wavelength (nm)	Osc.strength	Major Contribs	Minor Contribs
S1	493.332	0.0001	H-2->LUMO (69%)	H-2->L+1 (28%)

S2	429.0556	1.3421	HOMO->LUMO (79%)	H-3->LUMO (7%)
S3	352.7991	0.0061	H-1->LUMO (74%)	H-1->L+1 (14%)
S4	349.6945	0	H-7->LUMO (65%)	H-7->L+1 (31%)
S5	302.7549	0.0311	H-4->LUMO (76%)	H-3->LUMO (11%)
S6	301.086	0.0001	H-13->LUMO (39%)	H-13->L+1 (19%)
S7	292.2432	0.1679	H-3->LUMO (29%)	HOMO->L+2 (30%)
S 8	288.3085	0.0026	HOMO->L+1 (55%)	HOMO->L+2 (19%)
S9	277.4502	0.108	H-3->LUMO (26%)	HOMO->L+1 (14%)
S10	257.3674	0.4737	H-1->L+2 (76%)	H-3->LUMO (2%)

Table S7 Experimental λ_{max} , calculated λ_{max} , (nm) and oscillator strengths (f) of **DC-Cl** in DCM solvent, calculated at B3LYP/6-311g (d,p):

DC		

State	Wavelength (nm)	Osc.strength	Major Contribs	Minor Contribs
S1				H-2->L+1 (29%)
				H-3->LUMO (3%)
	477.8732	0.0005	H-2->LUMO (63%)	
S2				H-3->LUMO (7%)
				H-1->LUMO (3%)
	411.6751	1.3667	HOMO->LUMO (78%)	
S3				H-7->L+1 (30%)
	349.1136	0	H-7->LUMO (67%)	HOMO->L+2 (6%)
S4				H-1->L+1 (14%)
	339.2737	0.0051	H-1->LUMO (71%)	HOMO->L+1 (4%)
S5				H-11->L+1 (29%)
	300.2184	0.0001	H-11->LUMO (67%)	HOMO->L+2 (43%)
S6				H-3->LUMO (7%)
	291.6863	0.0495	H-4->LUMO (74%)	HOMO->L+2 (18%)
S7				H-3->LUMO (17%)
	290.2727	0.1296	H-4->LUMO (11%)	HOMO->L+1 (24%)
S 8				HOMO->L+1 (42%)
	285.8162	0.0317	H-3->LUMO (10%)	H-3->LUMO (2%)
S9				HOMO->LUMO (12%)
	273.0027	0.132	H-3->LUMO (28%)	H-3->L+1 (3%)
S10				H-5->LUMO (2%)
	257.7152	0.4678	H-1->L+2 (76%)	H-6->L+1 (2%)

Table S8 Experimental λ_{max} , calculated λ_{max} , (nm) and oscillator strengths (f) of **DC** in DCM solvent, calculated at B3LYP/6-311g (d,p):

DC- NO ₂ NO ₂				
State	Wavelength (nm)	Osc.strength	Major Contribs	Minor Contribs

1				H-3->LUMO
	481.7352	0.188	H-2->LUMO (36%)	(23%)
2			HOMO->LUMO	H-3->LUMO
	424.6034	0.9951	(68%)	(13%)
3	358.9271	0.0082	H-1->LUMO (75%)	H-1->L+2 (11%)
4	348.6325	0.0006	H-7->LUMO (55%)	H-7->L+1 (20%)
5	347.655	0.0593	H-13->L+1 (10%)	H-12->L+1 (11%)
6				HOMO->L+1
	325.3837	0.0505	H-2->L+1 (12%)	(59%)
7	300.3129	0.001	H-15->LUMO (37%)	H-15->L+1 (19%)
8	299.4064	0.0024	H-13->L+1 (22%)	H-12->L+1 (18%)
9				H-2->LUMO
	293.0168	0.1681	H-3->L+2 (12%)	(24%)
10	291.8236	0.0232	H-3->L+1 (17%)	H-2->L+1 (11%)

Table S9 Experimental λ_{max} , calculated λ_{max} , (nm) and oscillator strengths (f) of **DC- NO₂NO₂** in DCM solvent, calculated at B3LYP/6-311g (d,p):

DC- BrNO ₂				
State	Wavelength	Osc.strength	Major Contribs	Minor Contribs

	(nm)			
1			H-3->LUMO	H-2->LUMO (41%), H-4-
	450.1477	0.0138	(35%)	>LUMO (3%)
2			HOMO->LUMO	H-3->LUMO (5%), H-2-
	379.935	1.2256	(81%)	>LUMO (2%)
3			H-1->LUMO	HOMO->L+2 (11%), H-6-
	323.558	0.0032	(67%)	>LUMO (3%)
4			H-9->LUMO	H-9->L+1 (18%), H-5->L+1
	317.5255	0.0415	(13%)	(11%)
5			HOMO->L+1	H-9->L+1 (2%), H-5-
	299.2041	0.0462	(63%)	>LUMO (5%)
6			H-12->L+1	H-5->LUMO (10%), H-2-
	285.2375	0.0451	(12%)	>L+1 (12%)
7			H-1->LUMO	HOMO->L+2 (54%), H-12-
	283.7102	0.0763	(10%)	>LUMO (2%)
8			H-3->LUMO	H-2->LUMO (23%), H-1-
	266.8967	0.3784	(22%)	>L+2 (17%)
9			H-12->LUMO	H-12->L+1 (19%), H-3-
	259.5332	0.0004	(12%)	>L+1 (11%)
10				H-5->LUMO (6%), H-4-
	256.4889	0.2626	H-1->L+2 (46%)	>LUMO (6%)

Table S10 Experimental λ_{max} , calculated λ_{max} , (nm) and oscillator strengths (f) of **DC-BrNO**₂ in DCM solvent, calculated at B3LYP/6-311g (d,p):

Frontier molecular orbital energies

Dyes	Experimental			Theoretical		
	$E_{{\rm HOMO}^a}$	$E_{\scriptscriptstyle LUMO^b}$	E ₀₋₀	Еномо	E_{lumo}	HLG
DC-ClCl	-6.30	-3.75	2.55	-6.08	-3.47	2.61
DC-Cl	-6.26	-3.95	2.31	-7.19	-2.58	4.61
DC	-6.29	-3.92	2.37	-7.20	-2.18	5.02
DC-NO ₂ NO ₂	-6.32	-3.90	2.42	-7.36	-2.56	4.80
DC-BrNO ₂	-6.25	-3.68	2.57	-5.94	-2.81	3.13

Table S11 Frontier molecular orbital energies calculated at B3LYP/6-311g (d,p) level of theory compared with experimental values.



Figure S26. The Cyclic voltammograms of the dyes (D1-D5) recorded in DCM, plotted together.

Z-scan calculations:

Z-Scan open aperture measurements were performed at 800 nm wavelength. The nonlinear absorption (α_2) and refractive index (n_2) coefficients were measured using the following equation (1-2) at 50 μ M concentration.

Where
$$L_{eff} = \frac{1 - e^{-\alpha_0 L}}{\alpha_0}$$
, and Z_0 Raleigh range

Cross-sections are calculated by using $\sigma_{2PA} = \frac{(h\nu)\beta}{NC}$ where N is Avogadro number, C concentration in mole per litre.

$$\sigma_{2PA} = \frac{2.3 \times 10^{-12} cm/W \times 2.483 \times 10^{-19} J}{5 \times 10^{-8} \frac{1}{cm^3} \times 6.023 \times 10^{23}}$$

$$\sigma_{2PA} = 1.89 \times 10^3 GM (1 \text{ GM} = 10^{-50} \text{ cm}^4 \text{s photon}^{-1})$$

$$4\Delta \phi \left(\frac{Z}{Z_0}\right)$$

$$T_{CA} = 1 \pm \frac{Y(Z_0)}{\left[\left(\frac{Z}{Z_0}\right)^2 + 9\right]\left[\left(\frac{Z}{Z_0}\right)^2 + 1\right]}$$
(2)

$$n_2$$
 is calculated from $n_2 = \frac{\Delta \Phi \lambda}{2\pi I_0 L_{eff}}$

Where $\Delta \Phi = 2$, $\lambda = 800$ nm, $Le_{ff} = 0.98$ mm $I_0 = 127$ GW/cm² $n_2 = 2.06 \times 10^{-14}$ cm²/W.

Total $\chi^{(3)} = \chi^{(3)}_{R} + \chi^{(3)}_{I}$

$$Re\chi^{(3)} = 2cn_0^2\varepsilon_0n_{2,} \quad Im\chi^{(3)} = \frac{C^2\varepsilon_0n_{0\beta}^2}{\omega}$$

$$\text{Rex}^{(3)} = 2.24 \times 10^{-20} \text{ m}^2/\text{v}^2$$
, $\text{Imx}^{(3)} = 1.59 \times 10^{-23} \text{ m}^2/\text{v}^2$,

Total $\chi^{(3)} = 2.23 \times 10^{-20} \text{ m}^2/\text{v}^2$

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