New Molecular Design Based on Hybridized Local and Charge Transfer Fluorescence for Highly Efficient (> 6%) Deep-Blue Organic Light Emitting Diodes

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Electronic Supplementary Information

1. Experimental section

1.1. General methods

All the chemicals and solvents were procured from commercial sources were used as received. All the column chromatography techniques employed to purify the compounds performed by using 100-200 mesh silica gel as stationary phase. The solvents used for analytical measurements were dried by standard experimental procedures. ^{1}H and ^{13}C NMR spectral data were collected either on an FT-NMR spectrometer operating at 500 and 125 MHz or 400 and 100 MHz, respectively. The chemical shift values are calibrated using Me4Si as an internal standard (0.00 ppm). Mass spectral (HRMS) data were recorded on an ESI TOF high-resolution mass spectrometer in positive mode. The elemental analysis data for carbon (C), hydrogen (H) and nitrogen (N) were collected on Vario EL III microanalyzer. Readily prepared solutions at room temperature were used for all analytical measurements. The electronic absorption and emission spectral measurements were performed on UV-vis spectrophotometer at room temperature. Fluorescence lifetime decay measurements were recorded in a 1 cm quartz cell on a Horiba Jobin Yvon "FluoroCube Fluorescence Lifetime System" equipped with NanoLEDs and LDs as the excitation source(s) and an automated polarization accessory (Model 5000 U-02). The solid state fluorescence was recorded for drop-cast films, which are made from the toluene solutions. Absolute PLQE were determined for solutions by using calibrated integrating sphere connected to spectrofluorimter. Thermal data were collected using thermogravimteric analyzer (TGA) performed under N_2 atmosphere at a heating rate of 10 °C/min. Electrochemical measurements were collected on CHI electrochemical analyzer with conventional three electrode configuration consisting of a glassy carbon working electrode, a platinum wire auxiliary electrode and a non aquous $Ag/AgNO_3$ acetonitrile reference electrode. Fc/Fc^+ internal standard were used to calibrate the peak potentials. The $E_{1/2}$ values were determined as $(E_p^a+E_p^c)/2$, where E_p^a and E_p^c are the anodic and cathodic peak potentials, respectively. The measurements were collected at room temperature in 1×10^{-4} M dichloromethane solution and the 0.1 M tetrabutylammonium perchlorate employed as supporting electrolyte.

1.2. Synthesis

The compound **C1** were obtained from our previous report for the comparison purpose.[1]

2,7-Dibromo-9-(2-ethylhexyl)-3,6-diiodo-9*H*-carbazole (**2**). A mixture of 2,7-dibromo-9-(2-ethylhexyl)-9*H*-carbazole (1.50 g, 3.43 mmol) and iodine (1.00 g, 3.77 mmol), potatium iodate (0.45 g, 2.07 mmol) was dissolved in aceticacid: H_2SO_4 (9:1). The reaction mixture was kept for reflux at 110 °C for 6 h. The progress of the reaction was examined by TLC. After completion of reaction, excess of iodine was removed by using aqueous sodium hydrogen sulphate. The reaction mixture was extracted with DCM, dried over anhydrous sodium sulphate and the evaporation of the volatiles gave a white residue. The crude product was purified by column chromatography using hexanes:DCM (3:1) as eluent to get the intermediate **2** (2.00 g, 85%) as a brown color solid. mp 154 – 160 °C. ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 8.42 (s, 2H), 7.63 (s, 2H), 3.98 (t, J = 7.0 Hz, 2H), 1.95 (t, J = 6.2 Hz, 1H), 1.36-1.23 (m, 8H), 0.91-0.85 (m, 6H). ^{13}C NMR ($CDCl_3$, 100.00 MHz, δ ppm): 141.39, 131.28, 126.62, 122.10, 113.20, 88.85, 47.67, 38.98, 30.63, 28.44, 24.21, 22.96, 14.01, 10.83. HRMS calcd for $C_{20}H_{21}Br_2I_2NNa$ $[M+Na]^+$ m/z 711.8007, found 711.8006. Elemental analysis (%): calcd for $C_{20}H_{21}Br_2I_2N$; C, 34.86; H, 3.07; N, 2.03, found: C, 34.61; H, 2.88; N, 1.94.

2,7-Dibromo-9-(2-ethylhexyl)-9*H*-carbazole-3,6-dicarbonitrile (**3**). A mixture of 2,7-dibromo-9-(2-ethylhexyl)-3,6-diiodo-9*H*-carbazole (0.81 g, 1.18 mmol), copper cyanide (0.36 g, 2.59 mmol) and 50 mL of DMF was refluxed at 160 °C under nitrogen atmosphere for 12 h. The progress of the reaction was monitored by TLC examination. After completion of reaction, excess of copper cyanide was removed by washing with aquous ammonia. The reaction mixture was extracted with DCM, dried over anhydrous sodium sulphate and the evaporation of the volatiles gave a light dark residue. The crude product was purified by column chromatography using hexanes:DCM (1:3) as eluent to get the intermediate **3** (0.30 g, 52%) as a white color solid. mp 170 – 175 °C. ^{1}H NMR (500 MHz, CDCl$_3$, δ ppm): 8.57 (s, 2H), 7.73 (s, 2H), 4.16-4.14 (m, 2H), 2.00-1.94 (m, 1H), 1.40-1.22 (m, 8H), 0.93 (t, J = 7.5 Hz, 3H), 0.87 (t, J = 6.5 Hz, 3H). ^{13}C NMR (CDCl$_3$, 100.00 MHz, δ ppm): 143.70, 127.03, 123.01, 121.26, 120.69, 120.01, 117.83, 114.44, 111.86, 107.30, 95.28, 48.20, 39.23, 30.55, 28.34, 24.17, 22.89, 13.93, 10.77. $C_{20}H_{21}Br_2N_3Na$ [M+Na]$^+$ m/z 509.9979, found 509.9976. Elemental analysis (%): calcd for $C_{22}H_{21}Br_2N_3$; C, 54.23; H, 4.34; N, 8.62, found: C, 53.97; H, 4.15; N, 8.52.

2,7-bis(4-(Diphenylamino)phenyl)-9-(2-ethylhexyl)-9*H*-carbazole-3,6-dicarbonitrile (**4**). A mixture of **3** (0.12 g, 0.25 mmol), (4-(diphenylamino)phenyl)boronic acid (0.20 g, 0.75 mmol), potassium carbonate (0.20 g, 1.50 mmol), $Pd(PPh_3)_2Cl_2$ (3 mol%) and PPh_3 (5 mol%) was suspended in DMF + H_2O (3:1) mixture and degassed with N_2 for 10 min. The reaction mixture was kept for heat at 90 °C for 24 h under inert atmosphere. After completion of reaction, washed with cold water and extracted with CHCl$_3$, dried over anhydrous sodium sulphate and evaporated to dryness. The crude product was purified on column chromatography using CHCl$_3$:hexanes (2:3) as eluent to get target compound **4** (0.12 g, 62%) in colour less solid. mp 165 – 170 °C. ^{1}H NMR (400 MHz, CDCl$_3$, δ ppm): 8.47 (s, 2H), 7.51-7.49 (m, 4H), 7.43 (s, 2H), 7.31-7.27 (m, 8H), 7.19-7.16 (m, 12H), 7.09-7.05 (m, 4H), 4.20 (t, J = 5.6 Hz, 2H), 2.07-2.06 (m, 1H), 1.40-1.26 (m, 8H), 0.93-0.79 (m, 6H). ^{13}C NMR (CDCl$_3$, 100.00 MHz, δ ppm): 148.40, 147.25, 143.89, 143.59, 131.79, 129.85, 129.44, 126.97, 125.05, 123.60, 122.24, 120.54, 119.91, 110.46, 102.85, 47.80, 39.18, 30.73, 28.52, 24.28, 22.95, 13.94, 10.84. $C_{58}H_{49}N_5Na$ [M+Na]$^+$ m/z 838.3886, found 838.3884. Elemental analysis (%): calcd for $C_{58}H_{49}N_5$; C, 85.37; H, 6.05; N, 8.58, found: C, 85.10; H, 5.96; N, 8.38.

1.3. Theoretical calculations

All the theoretical studies on the consider materials have been performed by using Gaussian 09 programme package on a HP computer workstation.[2] The ground state geometries of the compounds were optimized under vacuum without any symmetry constraints at the DFT level with Bakes's three parameter hybridized with Le et al.'s correlation functional (B3LYP) using 6-31G(d,p) basis set.[3] Further, vibrational analysis was performed to conform the optimized geometries of the dyes belong to minima. The lowest energy vertical transitions and their oscillator strengths for optimized geometries of model compounds in the ground state were approximated using TD-DFT computations at the same basis set and functional level. The singlet to triplet energy gap (ΔE_{ST}) for the compounds were estimated at B3LYP/6-31G(d,p) level.

1.4. OLED device fabrication

The solution processed electroluminescent devices were fabricated on a pre-cleaned glass substrate containing Indium Tin Oxide (ITO) (thickness: 125 nm) as anode, poly(3,4-ethylene-dioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS, thickness: 35 nm) as a hole-injection layer (HIL), the synthesized dyes as an emissive layer (EML), TPBi as an electron transport and hole blocking layer (ETL) (thickness: 35 nm), a 0.7 nm Lithium Fluoride (LiF) as an electron-injection layer (EIL) and 150 nm thick Al layer as a cathode. Firstly the aqueous solution of PEDOT:PSS was spin-coated at 4000 rpm for 20 s to form a 35 nm HIL layer. The compounds **4** were doped in 4,4'-bis(9*H*-carbazol-9-yl)biphenyl (CBP) and deposited by spin-coating at 2500 rpm for 20 s and served as emissive layer. Then the TPBi was coated onto it. Finally, LiF and Al cathode were thermally evaporated at 1.0×10^{-5} Torr.

1.5. References

1. R. K. Konidena, K. R. J. Thomas, S. Sahoo, D. K. Dubey and J. H. Jou, *J. Mater. Chem. C,* 2017, **5**, 709.

2. M. J. Frisch, G. H. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Snnengerg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, J. E., Jr. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudinm, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian 09, revision A.02; Gaussian, Inc.: Wallingford, CT, 2009.

3. a) A. D. Becke, *J. Chem. Phys.,* 1993, **98**, 1372; b) C. Lee, W. Yang and G. Parr, *Phys. Rev. B,* 1988, **37**, 785.

4. W. C. Chen, Y. Yuan, S. F. Ni, Z. L. Zhu, J. Zhang, Z. Q. Jiang, L. S. Liao, F. L. Wong and C. S. Lee, *ACS Appl. Mater. Interfaces*, 2017, **9**, 7331.

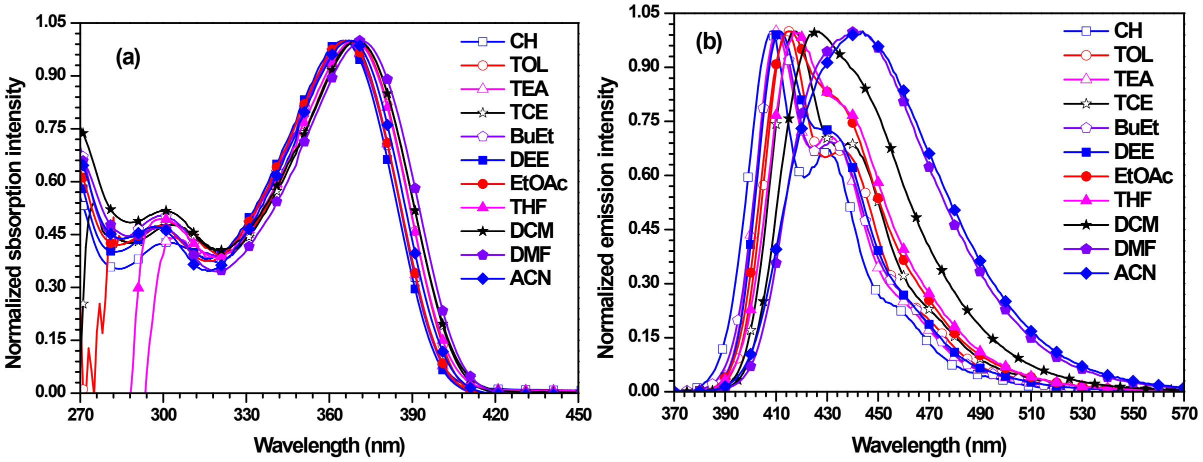

Figure S1. (a) Absorption and (b) emission spectra of **C1** recorded in various solvents.

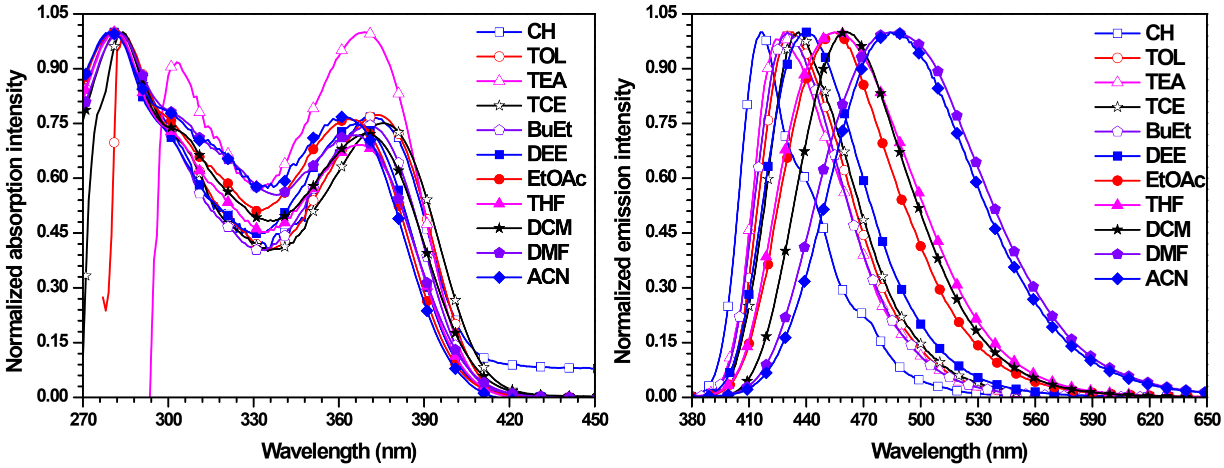

Figure S2. (a) Absorption and (b) Emission spectra of **4** recorded in different solvents.

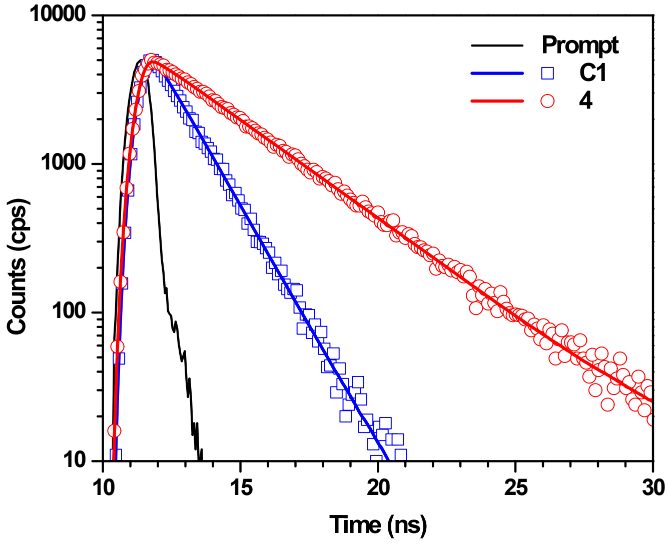

Figure S3. Time-resolved fluorescence decay profiles (excitation at 360 nm) for the dyes in toluene solution.

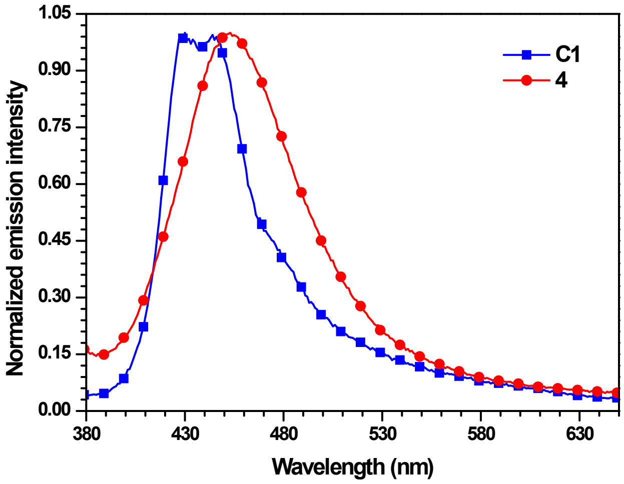

Figure S4. Emission spectra of the dyes recorded in drop-cast thin film.

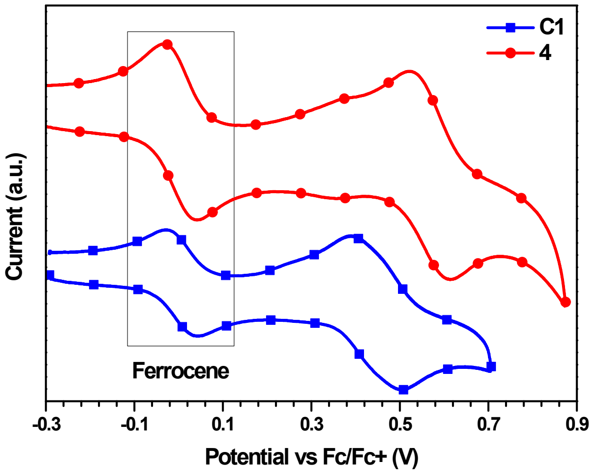

Figure S5. Cyclic voltammograms of the dyes.

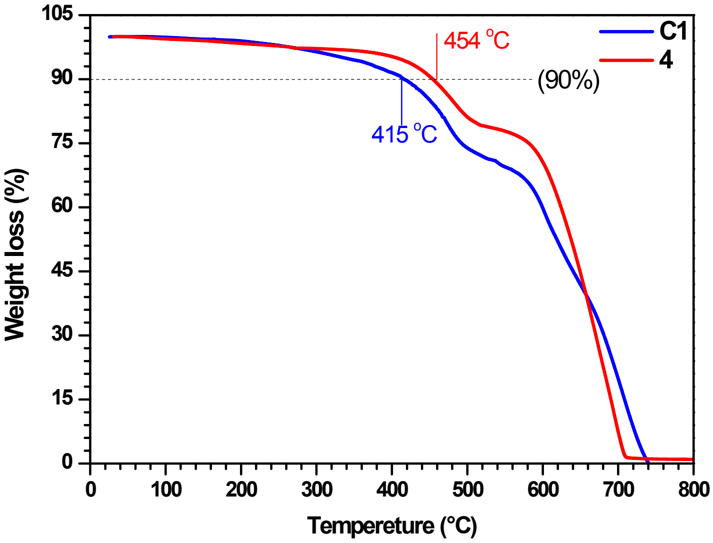

Figure S6. Thermogravimetric traces observed for the dyes.

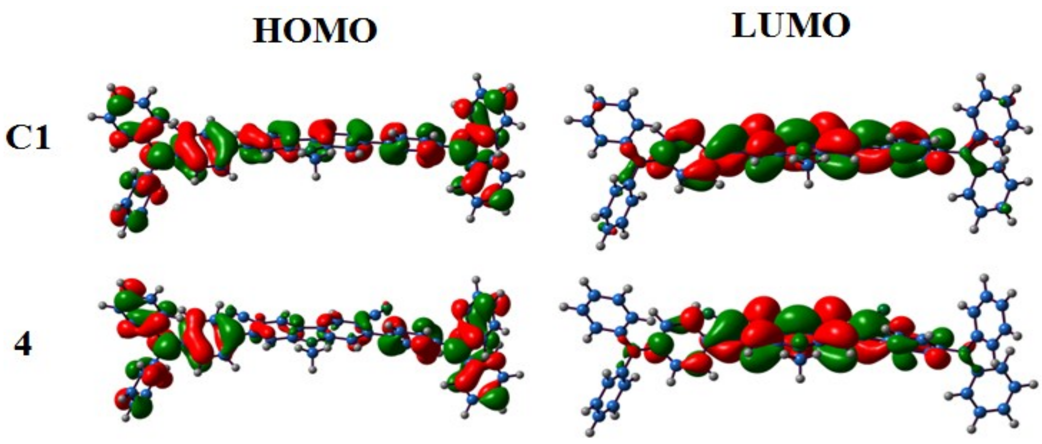

Figure S7. Frontier molecular orbitals (HOMO and LUMO) for the model compounds **C1** and **4**.

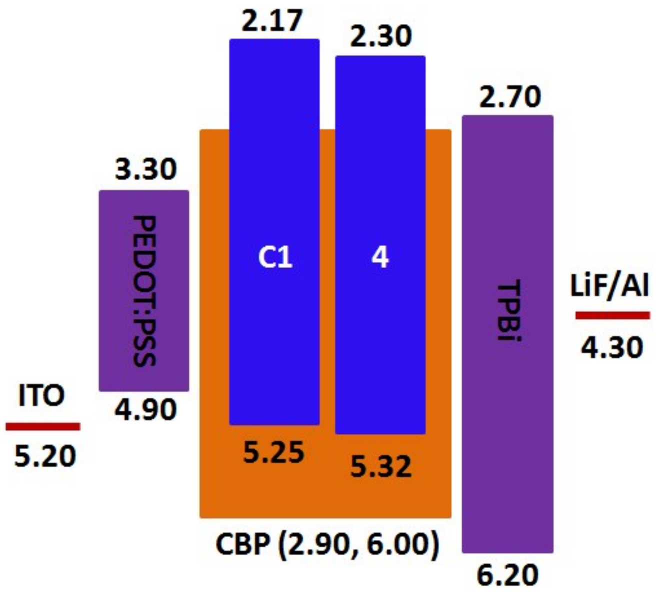

Figure S8. Energy level diagram of the materials used for the fabrication of OLED devices (all the values are in eV relative to vaccum level).

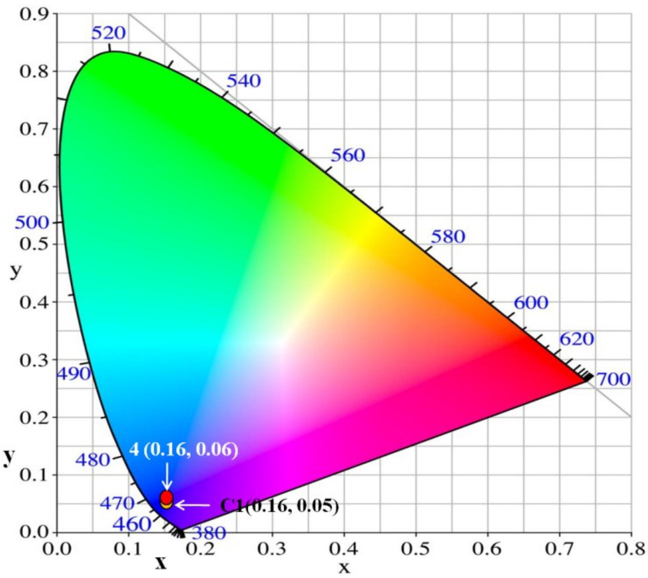

Figure S9. CIE chromatogram of dyes C1 and 4 in 1 wt% of the device

Table S1. Absorption, emission and Stokes shift data of the dyes recorded in different solvents.

Solvent	$f(\varepsilon,n)^a$	**C1**			**4**		
		λ_{abs} (nm)	λ_{em} (nm)	Stokes shift (cm^{-1})	λ_{abs} (nm)	λ_{em} (nm)	Stokes shift (cm^{-1})
Cyclohexane (CH)	-0.02	302, 367	408, 430 (sh)	2738	281, 371	416, 438 (sh)	2916
Toluene (TOL)	0.014	301, 369	411, 437 (sh)	3004	285, 373	432	3662
Triethylamine (TEA)	0.048	302, 366	410, 430 (sh)	2932	303, 369	428	3736
Chloroform ($CHCl_3$)	0.14	303, 369	421, 439 (sh)	3347	281, 373	449	4538
Diethylether (DEE)	0.16	301, 365	411, 432 (sh)	3266	282, 366	440	4595
Trichloroethylene (TCE)	0.08	303, 370	417, 440 (sh)	3046	283, 374	436	3802
Butylether (BuEt)	0.10	302, 366	411, 431 (sh)	2992	281, 370	430	3771
Ethylacetate (EtOAc)	0.19	301, 366	415, 438 (sh)	3226	280, 370	455	5044
Tetrahydrofuran (THF)	0.21	301, 369	417, 440 (sh)	3119	281, 368	457	5292
Dichloromethane (DCM)	0.22	302, 371	426, 440 (sh)	3480	281, 369	460	5361
N,N-Dimethylformamide (DMF)	0.27	301, 372	441	4206	282, 364	484	6811

Acetonitrile (ACN)	0.30	302, 372	444	4325	281, 361	484	7040

[a] $f(\varepsilon,n)$ values for the solvents were calculated according to reference 4.

Table S2. Computed vertical transitions and oscillator strengths of the dyes.

Dye	λ_{max} (nm)	f	Configuration	HOMO (eV)	LUMO (eV)	E_g (eV)
C1	385	1.60	HOMO → LUMO (+96%)	-4.77	-1.13	3.63
4	412	1.00	HOMO → LUMO (+97%)	-5.06	-1.66	3.40

Table S3. Electroluminescent data of the dyes.

Dye	Conc. [wt%]	Driving voltage (V)	Power efficiency (lm/W)	Current efficiency (cd/A)	EQE (%)	Max. Luminance (cd/m^2)	EL max. (FWHM) (nm)	CIE (x,y)
C1	1	6.0	0.5	0.9	2.7	832	420 (46)	0.16, 0.05
	3	6.6	0.5	1.1	3.0	1019	420 (44)	0.16, 0.05
	5	6.6	0.5	1.1	2.8	960	420 (45)	0.16, 0.05
4	1	5.1	1.5	2.5	6.5	1438	428 (48)	0.16, 0.06
	3	5.2	1.8	3.0	5.7	2112	432 (55)	0.16, 0.07
	5	5.2	2.3	3.8	4.8	2218	436 (56)	0.16, 0.08

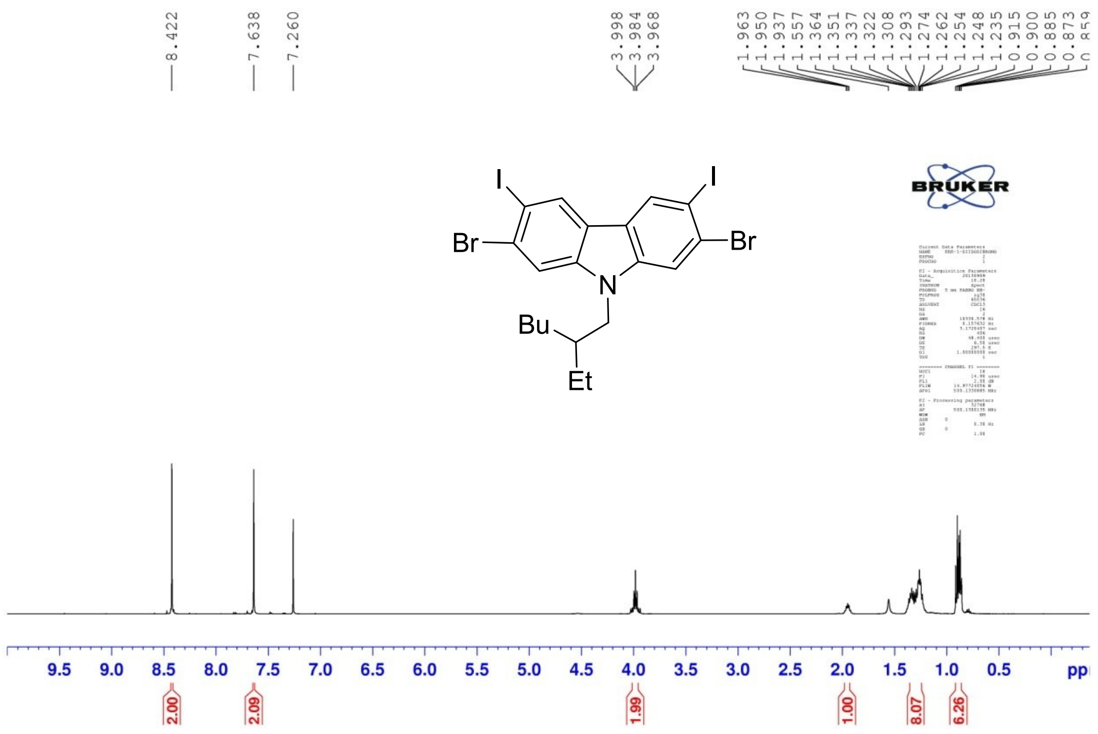

Figure S10. ^{1}H NMR spectrum of **2** recorded in $CDCl_3$.

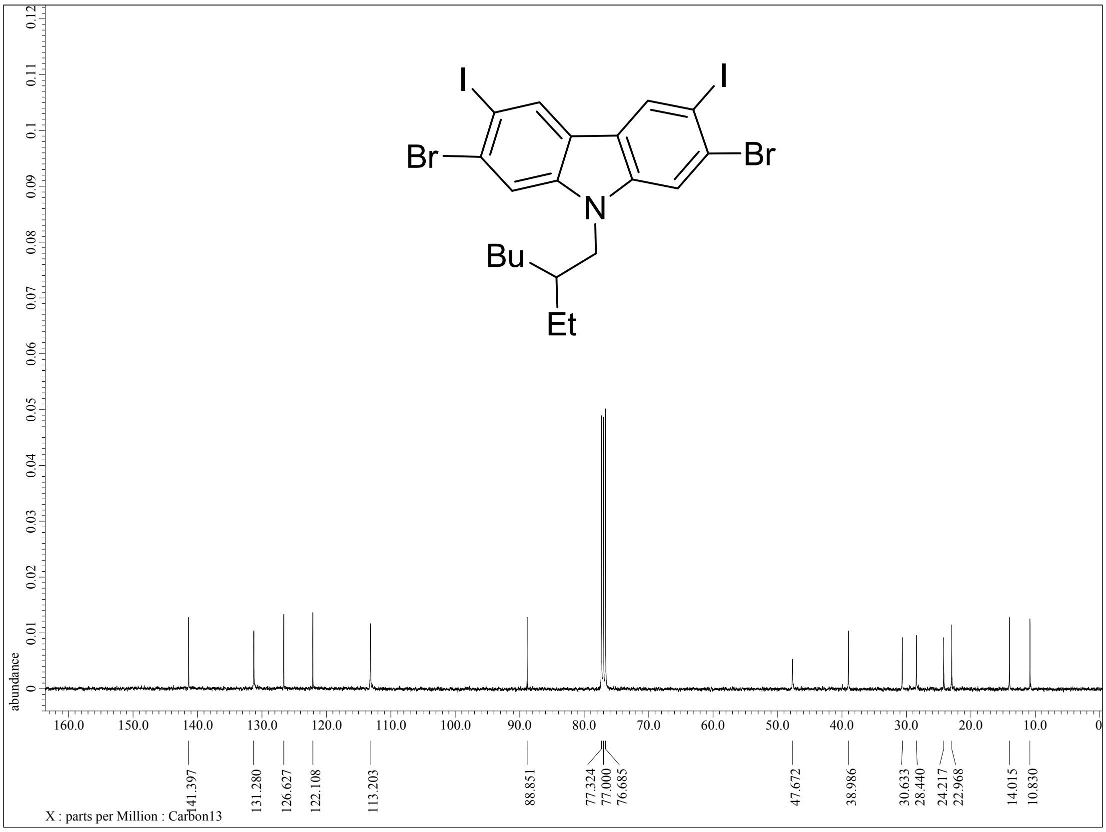

Figure S11. ^{13}C NMR spectrum of **2** recorded in CDCl$_3$.

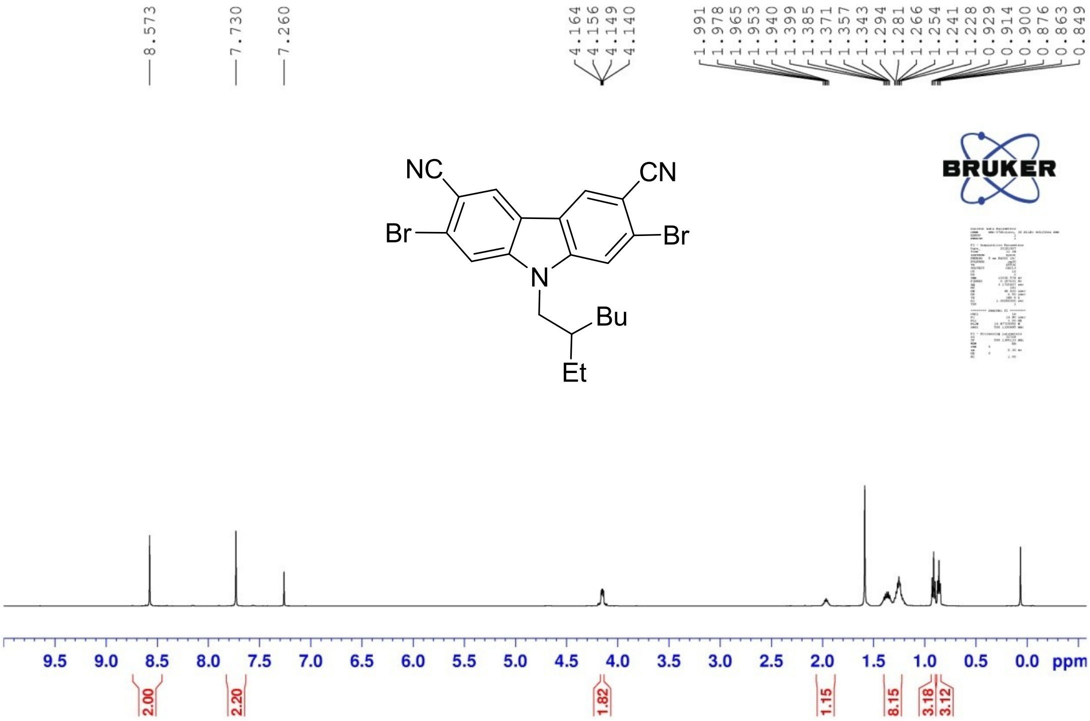

Figure S12. ^{1}H NMR spectrum of **3** recorded in CDCl$_3$.

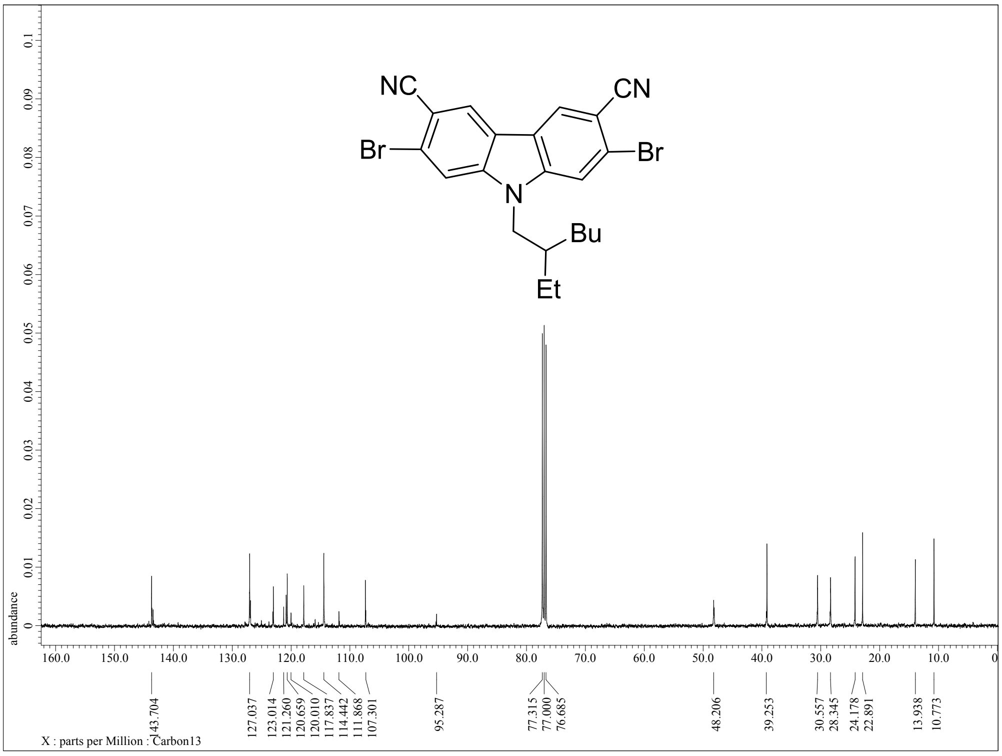

Figure S13. ^{13}C NMR spectrum of **3** recorded in CDCl$_3$.

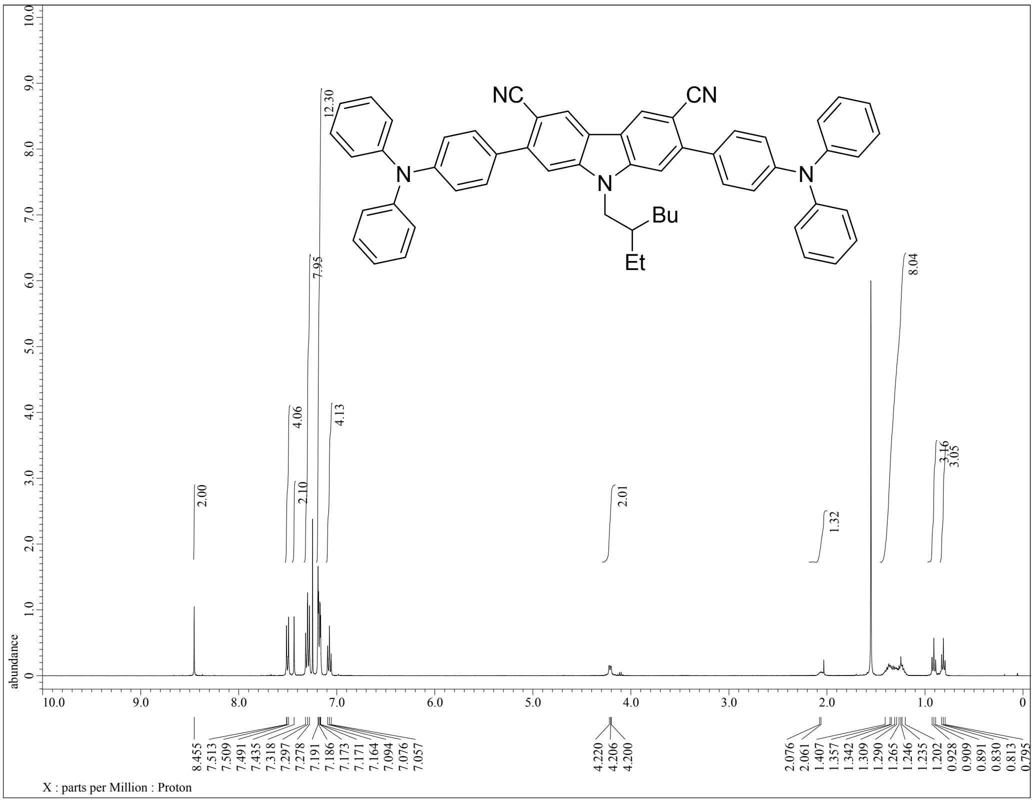

Figure S14. ^{1}H NMR spectrum of **4** recorded in CDCl$_3$.

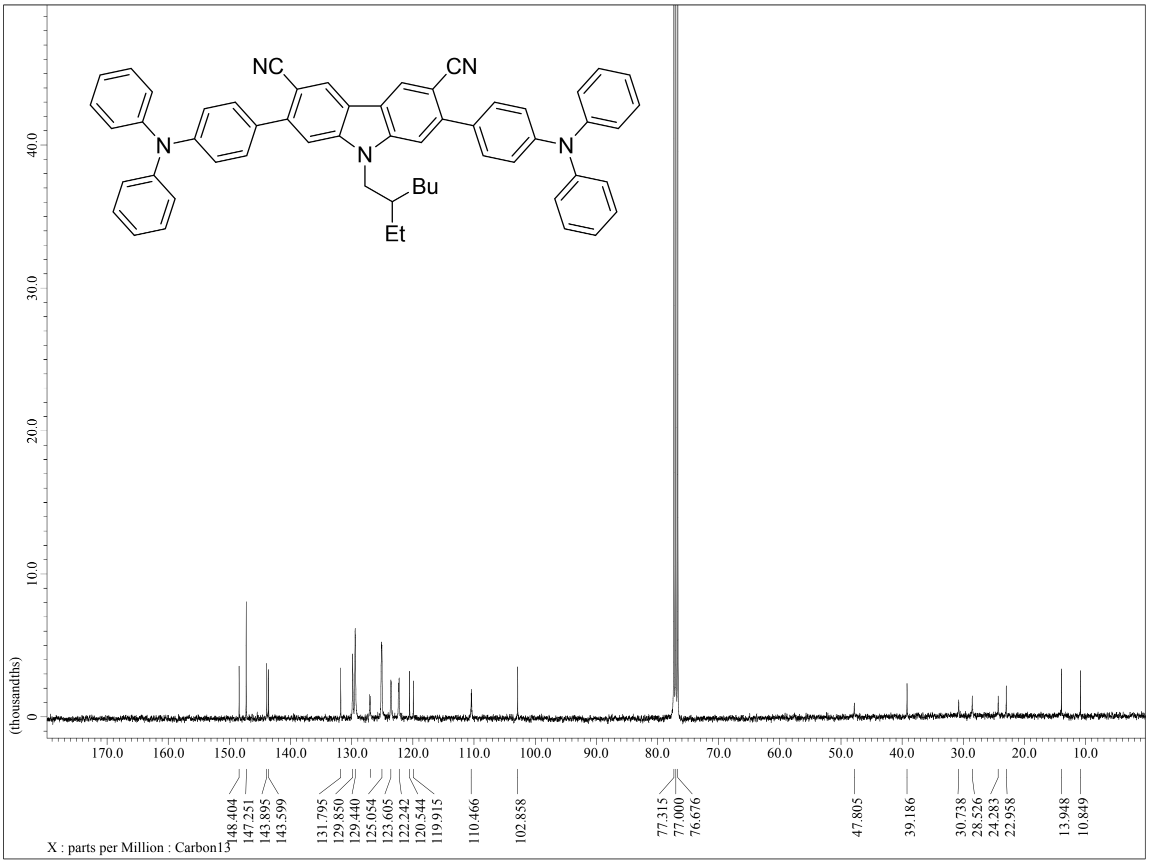

Figure S15. ^{13}C NMR spectrum of **4** recorded in $CDCl_3$.

Table S4. Cartesian coordinates of the optimized geometry of **4**.

Energy = -2238.33394921 au

At. NO	X	Y	Z
6	3.053220000	-0.073123000	2.358087000
6	3.461106000	-0.051291000	0.988841000
6	2.473793000	-0.044716000	-0.004382000
6	1.127938000	-0.059091000	0.359972000
6	0.722940000	-0.059182000	1.721370000
6	1.695837000	-0.071038000	2.714957000
1	1.423996000	-0.089599000	3.765094000
6	-1.128317000	-0.034620000	0.359304000
6	-2.473971000	-0.018364000	-0.005544000
6	-3.461465000	-0.019090000	0.987281000
6	-3.054453000	-0.024486000	2.356868000
6	-1.697345000	-0.040672000	2.714282000
6	-0.724089000	-0.045466000	1.720973000
1	-1.425832000	-0.034747000	3.764648000
7	-0.000008000	-0.059791000	-0.448849000
6	0.001623000	-0.029010000	-1.898297000
1	-0.884784000	-0.542328000	-2.276343000
1	0.880046000	-0.557629000	-2.273928000
1	2.774252000	0.006910000	-1.044707000

1	-2.774884000	-0.028326000	-1.047041000
1	0.011371000	0.996079000	-2.287165000
6	4.888054000	-0.039396000	0.581767000
6	5.333964000	-0.867736000	-0.462726000
6	5.831410000	0.810704000	1.183080000
6	6.655338000	-0.850788000	-0.891579000
1	4.634911000	-1.548485000	-0.939795000
6	7.157398000	0.827514000	0.768236000
1	5.529251000	1.470773000	1.988604000
6	7.594125000	-0.002667000	-0.278662000
1	6.969495000	-1.502331000	-1.699455000
1	7.863692000	1.488454000	1.257791000
7	8.942734000	0.010804000	-0.703673000
6	9.579008000	-1.196877000	-1.111408000
6	9.683926000	1.226729000	-0.714055000
6	10.380733000	-1.220316000	-2.262984000
6	9.421023000	-2.374460000	-0.364209000
6	11.001751000	1.258092000	-0.232561000
6	9.112288000	2.406744000	-1.215227000
6	11.015349000	-2.398271000	-2.652079000
1	10.503425000	-0.312900000	-2.844871000
6	10.045040000	-3.551946000	-0.771646000
1	8.810920000	-2.359062000	0.532754000
6	11.730892000	2.445145000	-0.259758000
1	11.446802000	0.350050000	0.160020000
6	9.843023000	3.593111000	-1.220965000
1	8.096928000	2.386905000	-1.596945000
6	10.848208000	-3.571395000	-1.913709000
1	11.633432000	-2.400095000	-3.545318000
1	9.913863000	-4.454809000	-0.182228000
6	11.156632000	3.620105000	-0.748532000
1	12.749461000	2.452472000	0.117366000
1	9.385846000	4.497901000	-1.611190000
1	11.339020000	-4.488892000	-2.223236000
1	11.725174000	4.544769000	-0.761190000
6	-4.888555000	-0.002118000	0.580193000
6	-5.841835000	-0.855714000	1.160385000
6	-5.324321000	0.858268000	-0.442314000
6	-7.168100000	-0.845852000	0.745977000
1	-5.547161000	-1.539380000	1.948897000
6	-6.646126000	0.868546000	-0.870256000
1	-4.617187000	1.542538000	-0.902144000
6	-7.594767000	0.016256000	-0.278884000
1	-7.882468000	-1.510356000	1.218790000
1	-6.952917000	1.544749000	-1.660543000
7	-8.943827000	0.030581000	-0.703368000
6	-9.697383000	-1.176462000	-0.753417000
6	-9.566143000	1.258042000	-1.071635000
6	-11.018546000	-1.208276000	-0.280874000
6	-9.134803000	-2.347490000	-1.285172000

6	-10.367569000	1.328549000	-2.221495000
6	-9.393753000	2.408699000	-0.286587000
6	-11.759550000	-2.386377000	-0.347127000
1	-11.456952000	-0.307566000	0.135332000
6	-9.877548000	-3.525509000	-1.329768000
1	-8.117018000	-2.327266000	-1.660270000
6	-10.988033000	2.526116000	-2.571636000
1	-10.501053000	0.442066000	-2.832519000
6	-10.003520000	3.606259000	-0.655139000
1	-8.783683000	2.356554000	0.608975000
6	-11.194328000	-3.552644000	-0.866301000
1	-12.780512000	-2.393981000	0.023481000
1	-9.427106000	-4.423263000	-1.743393000
6	-10.806531000	3.672489000	-1.795564000
1	-11.606195000	2.564548000	-3.463991000
1	-9.861374000	4.487865000	-0.036802000
1	-11.772204000	-4.470585000	-0.909213000
1	-11.286242000	4.605439000	-2.074843000
6	-4.009606000	0.038490000	3.423748000
7	-4.743445000	0.092142000	4.325998000
6	4.007826000	-0.144489000	3.424907000
7	4.740969000	-0.206881000	4.327173000