Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

The Effect of the Polyaromatic Hydrocarbon in the Spectral and Photophysical Properties of Diaryl-Pyrrole Derivatives: an Experimental and Theoretical Study

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1. Room temperature absorption and fluorescence emission spectra for compounds 1a and 1c in ethanol.

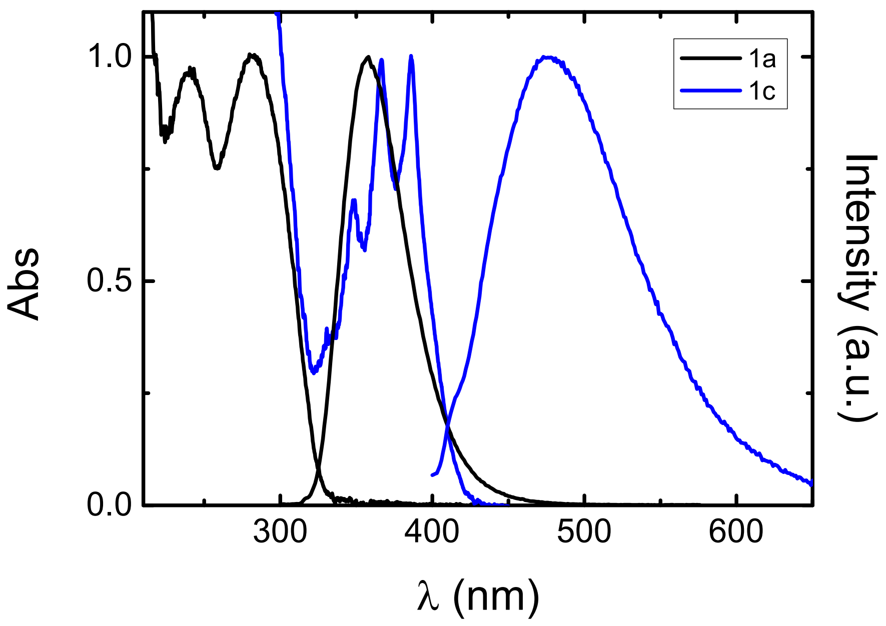
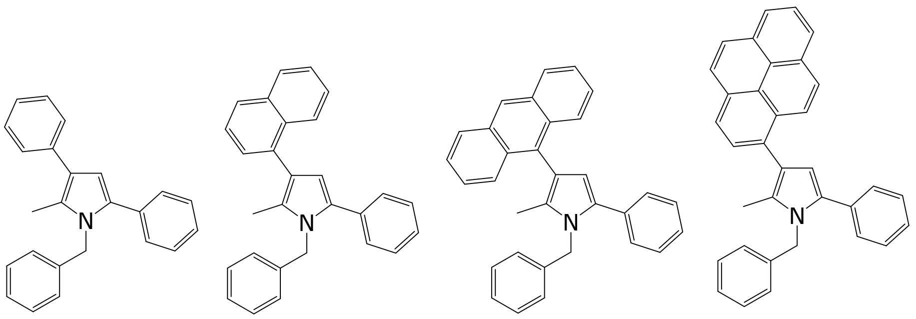


Figure S1- Room temperature absorption and fluorescence emission spectra for compounds **1a** and **1c** in ethanol.

2. Solid-Supported Synthesis of 3,5-Diaryl-2-Methyl-1*H*-Pyrroles Under Focused Microwave Irradiation

3,5-diaryl-2-methyl-1H-pyrrole synthetized under focused microwave irradiation and yields of reaction are presented in Scheme S1.



1a *28%* **1b** *19%* **1c** *19%* **1d** *11%*

Scheme S1. Structures and isolated yields of 3,5-diaryl-2-methyl-1*H*-pyrroles **1a-d** synthesized under focused microwave irradiation.

3. Synthesis

3.1 Materials and instrumentation

All solvents were commercially available and were purified following standard methods prior to use.[1] All reagents were commercially available and were used without any additional purification. SiO_2 60 (35-70 µm, Acros Organics) was previously dried in an oven at 120 ºC for 24 hours before being used as a solid-support. Microwave-assisted reactions were carried-out in a single-mode CEM Discover S-Class reactor, with continuous monitoring of temperature, pressure and microwave power. Melting points (uncorrected) were determined in an Ernst Leitz 799 heated-plate microscope, using an Ama-Digit ad1700th digital thermometer. The elemental analysis was accomplished in a Fisons Instruments EA-1108 CHNS-O analyser. NMR spectra were registered in a Bruker Avance III spectrometer operating at 400 MHz (^1H) or 100 MHz (^{13}C). GC-MS spectra were registered in an Hewlett-Packard 5973 MSD spectrometer with EI ionization, coupled to a Hewlett-Packard Agilent 6890 chromatograph equipped with an HP-5 MS column (30 m x 0.25 mm x 0.25 µm). HR-MS spectra were obtained in a Waters-Micromass VG Autospec M with ESI ionization.

3.2 General Procedure

The synthesis of pyrroles could be achieved using classical methodologies such as the Knorr[2] or Hantzsch[3] synthesis. Ranu and co-workers described a microwave-assisted synthesis of pyrroles using silica gel[4] or alumina oxide[5] as solid support. In fact, using a microwave domestic oven these author synthetized a series of pyrroles with alkyl substituents at positions 4 and 5 and a few aryl substituted pyrroles, including compound **1a,** in 65% yield. Following this methodology we use SiO_2 60 (200-500 μm), SiO_2 60 (35-70 μm), SiO_2 N (2-20 μm), Montmorillonite K-10, and alumine oxide (507C-I) as solid support and a single-mode CEM Discover S-Class reactor. The best results were obtained using SiO_2 60 (35-70 μm), and the increase of the reaction time, temperature or MW power did not allow the formation of the desired products in higher yields. However, the simplicity of the synthetic methodology and work-up procedure make this a suitable approach for the synthesis of the oligomers.

3.3 Pyrrole Synthesis

A mixture of the selected chalcone* (5 mmol), benzylamine (5 mmol, 0.56 mL), nitroethane (15 mmol, 1.12 mL) and SiO_2 60 (8 g) in diethyl ether (50 mL) is stirred at room temperature for 5 minutes in a 100 mL round-bottomed flask, followed by evaporation of the solvent. The reaction mixture is heated at 100 ºC for 10 minutes under focused microwave irradiation with an initial power setting of 200 W. After cooling to room temperature, the crude product mixture is washed with diethyl ether (50 mL) and filtered under reduced pressure. The solution is evaporated and the resulting yellow residue is purified through SiO_2 60 flash column chromatography (8x2 cm), using an *n*-hexane/diethyl ether (9:1 v/v) solvent mixture as the eluent. The pyrrole containing fraction is collected, evaporated under reduced pressure and recrystallized in methanol, yielding the desired

3,5-diaryl-2-methyl-1*H*-pyrrole as a white or yellowish solid (**1a-d**, Figure1).

*The chalcones needed for the synthesis of 3,5-diaryl-2-methyl-1*H*-pyrroles **1a-d** were previously prepared following an adaptation to the procedure described by Kohler and Chadwell.[6] Briefly, a solution of sodium hydroxide (63 mmol, 2.486 g) in ethanol/distilled water (1:1 v/v, 50 mL) is magnetically stirred at room temperature in a 100 mL round-bottomed flask. This is placed in a water bath and the selected acetophenone (50 mmol) is added, followed by the appropriate aryl aldehyde (50 mmol). The reaction mixture is left under vigorous stirring, at a temperature between 20 and 30 ºC, until a yellow solid precipitates. This is filtered under reduced pressure, thoroughly washed with distilled water and recrystallized in aqueous ethanol, yielding the desired chalcone as a yellowish solid (**2a-d**).

3.4 Analytical Characterization of 1a-1d

1-Benzyl-2-methyl-3,5-diphenyl-1*H*-pyrrole, 1a. Yield: 28%, 460 mg (white solid); mp (ºC): 115-116; $C_{24}H_{21}N$: Calculated (%) = C 89.12, H 6.54, N 4.33; Found (%) = C 89.47, H 6.78, N 4.11; ^{1}H NMR (400 MHz, $CDCl_3$): *δ*, ppm = 7.466 (2H, d, J = 7.6, Ph), 7.386 (2H, d, J = 7.2, Ph), 7.377-7.279 (6H, m, Ph), 7.256-7.192 (3H, m, Ph), 6.993 (2H, d, J = 7.2, Ph), 6.449 (1H, s, CH), 5.183 (2H, s, CH_2), 2.262 (3H, s, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): *δ,* ppm = 138.810 (C), 137.146 (C), 134.346 (C), 133.396 (C), 128.783 (2xCH), 128.734 (2xCH), 128.422 (2xCH), 128.342 (2xCH), 128.054 (2xCH), 127.049 (CH), 126.896 (CH), 126.668 (C), 125.658 (2xCH), 125.266 (CH), 122.478 (C), 108.611 (CH), 47.971 (CH_2), 11.374 (CH_3); GC-MS (EI): m/z (t_R, min) = 323 (16.61) (M^+).

1-Benzyl-2-methyl-3-(naphthalen-1-yl)-5-phenyl-1*H*-pyrrole, 1b. Yield: 19%, 350 mg (yellow solid); mp (ºC): 101-103; ^{1}H NMR (400 MHz, CDCl$_3$): *δ,* ppm = 8.126 (1H, d, J = 7.6, Ph), 7.863 (1H, d, J = 7.6, Ph), 7.776 (1H, d, J = 7.2, Ph), 7.507-7.435 (4H, m, Ph), 7.392 (2H, d, J = 7.2, Ph), 7.350-7.282 (4H, m, Ph), 7.261-7.211 (2H, m, Ph), 7.038 (2H, d, J = 7.6, Ph), 6.470 (1H, s, CH), 5.240 (2H, s, CH$_2$), 2.028 (3H, s, CH$_3$); ^{13}C NMR (100 MHz, CDCl$_3$): *δ*, ppm = 139.036 (C), 135.151 (C), 133.953 (C), 133.943 (C), 133.503 (C), 132.755 (C), 128.808 (2xCH), 128.666 (2xCH), 128.450 (2xCH), 128.165 (2xCH), 127.740 (CH), 127.056 (CH), 126.811 (CH), 126.780 (CH), 126.581 (C), 125.642 (2xCH), 125.528 (CH), 125.462 (CH), 125.402 (CH), 120.724 (C), 110.915 (CH), 48.052 (CH$_2$), 11.194 (CH$_3$); HR-MS (ESI): m/z = 374.18940 ([M+H]$^+$, $C_{28}H_{24}N$ required 374.19033).

3-(Anthracen-9-yl)-1-benzyl-2-methyl-5-phenyl-1*H*-pyrrole, 1c Yield: 19%, 400 mg (yellow solid); mp (ºC): 161-163; ^{1}H NMR (400 MHz, CDCl$_3$): *δ*, ppm = 8.426 (1H, s, Ph), 8.074 (2H, d, J = 8.4, Ph), 8.016 (2H, d, J = 8.4, Ph), 7.456 (2H, d, J = 7.6, Ph), 7.423-7.211 (10H, m, Ph), 7.107 (2H, d, J = 7.6, Ph), 6.483 (1H, s, CH), 5.326 (2H, s, CH$_2$), 1.795 (3H, s, CH$_3$); ^{13}C NMR (100 MHz, CDCl$_3$): *δ*, ppm = 139.189 (C), 134.274 (C), 133.582 (C), 132.549 (C), 131.615 (2xC), 131.255 (2xC), 129.529 (C), 128.844 (2xCH), 128.626 (2xCH), 128.504 (2xCH), 128.374 (2xCH), 127.547 (2xCH), 127.109 (CH), 126.735 (CH), 125.844 (CH), 125.655 (2xCH), 124.960 (4xCH), 117.939 (C), 112.109 (CH), 48.115 (CH$_2$), 11.119 (CH$_3$); HR-MS (ESI): m/z = 424.20548 ([M+H]$^+$, $C_{32}H_{26}N$ required 424.20598).

1-Benzyl-2-methyl-5-phenyl-3-(pyren-1-yl)-1*H*-pyrrole, 1d. Yield: 11%, 235 mg (yellow solid); mp (ºC): 167-169; ^{1}H NMR (400 MHz, $CDCl_3$): *δ*, ppm = 8.331 (1H, d, J = 8.8, Ph), 8.196 (1H, d, J = 7.6, Ph), 8.149 (2H, t, J = 6.4, Ph), 8.092-7.998 (4H, m, Ph), 7.979 (1H, t, J = 7.6, Ph), 7.450 (2H, d, J = 7.6, Ph), 7.405-7.239 (6H, m, Ph), 7.105 (2H, t, J = 7.6, Ph), 6.597 (1H, s, CH), 5.308 (2H, s, CH_2), 2.090 (3H, s, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): *δ*, ppm = 138.997 (C), 134.275 (C), 133.452 (C), 132.995 (C), 131.517 (C), 131.162 (C), 129.845 (C), 129.295 (C), 128.870 (2xCH), 128.718 (3xCH), 128.505 (C+2xCH), 127.497 (CH), 127.124 (CH), 126.876 (CH), 126.828 (CH), 126.786 (CH), 126.334 (C), 125.782 (CH), 125.692 (2xCH), 125.109 (C), 125.036 (C), 124.672 (CH), 124.527 (CH), 124.488 (CH), 121.324 (C), 111.151 (CH), 48.143 (CH_2), 11.379 (CH_3); HR-MS (ESI): m/z = 448.20583 ($[M+H]^+$, $C_{34}H_{26}N$ required 448.20598).

(*E*)-1,3-Diphenyl-prop-2-en-1-one, 2a. Yield: 85%, 8.850 g (pale-yellow solid); mp (ºC): 53-55 (Lit., 55-57);[3] $C_{15}H_{12}O$: Calculated (%) = C 86.51, H 5.81; Found (%) = C 86.25, H 5.55; ^{1}H NMR (400 MHz, $CDCl_3$): *δ*, ppm = 8.020 (2H, d, J = 7.6, Ph), 7.811 (1H, d, J = 16, CH), 7.643-7.626 (2H, m, Ph), 7.582 (1H, d, J = 7.2, Ph), 7.531 (1H, d, J = 16, CH), 7.482 (2H, d, J = 7.2, Ph), 7.410-7.396 (3H, m, Ph); ^{13}C NMR (100 MHz, $CDCl_3$): *δ*, ppm = 190.490 (C), 144.814 (CH), 138.152 (C), 134.826 (C), 132.787 (CH), 130.543 (CH), 128.943 (2xCH), 128.612 (2xCH), 128.486 (2xCH), 128.441 (2xCH), 122.001 (CH); GC-MS (EI): m/z (t_R, min) = 208 (11.69) (M^+).

(*E*)-3-(Naphthalen-1-yl)-1-phenyl-prop-2-en-1-one, 2b. Yield: 81%, 10.400 g (yellow solid); mp (ºC): 79-81; ^{1}H NMR (400 MHz,

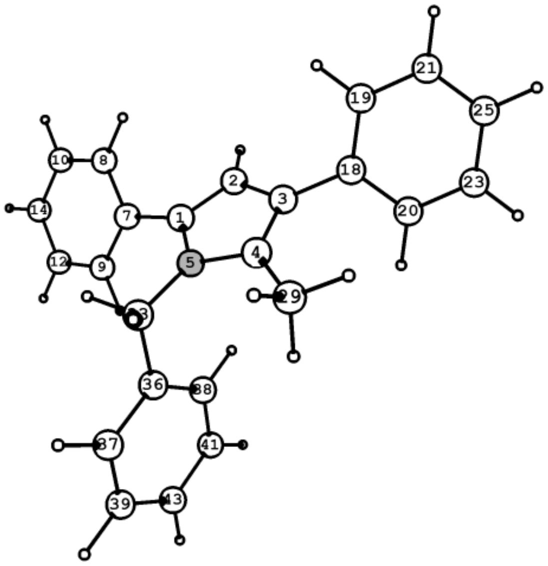
$CDCl_3$): *δ*, ppm = 8.654 (1H, d, J = 15.6, CH), 8.219 (1H, d, J = 8.4, Ph), 8.060 (2H, d, J = 7.6, Ph), 7.889-7.837 (3H, m, Ph), 7.596 (1H, d, J = 15.6, CH), 7.558 (2H, d, J = 7.6, Ph), 7.548-7.458 (4H, m, Ph); ^{13}C NMR (100 MHz, $CDCl_3$): *δ*, ppm = 190.292 (C), 141.731 (CH), 138.196 (C), 133.771 (C), 132.962 (CH), 132.358 (C), 131.805 (C), 130.898 (CH), 128.828 (CH), 128.745 (2xCH), 128.652 (2xCH), 127.035 (CH), 126.361 (CH), 125.507 (CH), 125.149 (CH), 124.616 (CH), 123.521 (CH); GC-MS (EI): m/z (t_R, min) = 258 (15.57) (M^+).

(*E*)-3-Anthracen-9-yl)-1-phenyl-prop-2-en-1-one, 2c. Yield: 83%, 12.850 g (bright-yellow solid); mp (ºC): 118-120; ^{1}H NMR (400 MHz, $CDCl_3$): *δ*, ppm = 8.785 (1H, d, J = 16, CH), 8.442 (1H, s, Ph), 8.289 (2H, d, J = 8.4, Ph), 8.078 (2H, d, J = 7.2, Ph), 8.010 (2H, d, J = 7.2, Ph), 7.613-7.576 (2H, m, Ph), 7.543 (1H, d, J = 16, CH), 7.506-7.467 (5H, m, Ph); ^{13}C NMR (100 MHz, $CDCl_3$): *δ*, ppm = 189.648 (C), 141.892 (CH), 137.834 (C), 133.091 (CH), 131.256 (2xC), 130.963 (CH), 130.107 (C), 129.585 (2xC), 128.896 (2xCH), 128.744 (2xCH), 128.704 (2xCH), 128.424 (CH), 126.416 (2xCH), 125.405 (2xCH), 125.262 (2xCH); GC-MS (EI): m/z (t_R, min) = 308 (24.11) (M^+).

(*E*)1-Phenyl-3-(pyren-1-yl)prop-2-en-1-one, 2d. Yield: 85%, 14.125 g (bright-yellow solid); mp (ºC): 155-157; ^{1}H NMR (400 MHz, $CDCl_3$): *δ*, ppm = 8.973 (1H, d, J = 15.6, CH), 8.524 (1H, d, J = 8, Ph), 8.396 (1H, d, J = 8, Ph), 8.210 (2H, d, J = 7.2, Ph), 8.180-8.101 (5H, m, Ph), 8.061-8.001 (2H, d, Ph), 7.800 (1H, d, J = 15.6, CH), 7.622 (1H, t, J = 7.2, Ph), 7.551 (2H, t, J = 7.2, Ph); ^{13}C NMR (100 MHz, $CDCl_3$): *δ*, ppm = 190.234 (C), 141.465 (CH), 138.427 (C), 132.943 (C), 132.834 (CH), 131.300 (C), 130.715 (C), 130.350 (C), 128.708 (4xCH+C), 128.599 (2xCH), 127.320 (CH), 126.315

(CH), 126.065 (CH), 125.921 (CH), 125.032 (CH), 124.975 (C), 124.597 (C), 124.186 (CH), 123.960 (CH), 122.578 (CH); GC-MS (EI): m/z (t_R, min) = 332 (21.31) (M^+).

4. Natural Bond Orbital analysis



Scheme S2. Atom numbering scheme adopted for diaryl-pyrrole **1a**.

Table S1- Second-order perturbation theory analysis of Fock matrix in NBO analysis (for selected orbital pairs of the diaryl-pyrrole **1a**.

Donor (i)	**ED/e** [a]	**Acceptor (j)**	**ED/e** [a]	**E(2)** [b] **(kcal mol^{-1})**	**E(j)-E(i)** [c] **(a.u.)**	**F(i,j)** [d] **(a.u.)**
π (C1=C2)	1.81662	π* (C3=C4)	0.36809	17.61	0.30	0.068
π (C3=C4)	1.78710	π* (C1=C2)	0.35702	17.90	0.29	0.067
π (C7=C9)	1.64130	π* (C8=C10)	0.31915	19.00	0.28	0.066
		π* (C12=C14)	0.33857	21.16	0.28	0.069
π (C8=C10)	1.67563	π* (C7=C9)	0.37839	19.76	0.28	0.068
		π* (C12=C14)	0.33857	19.61	0.28	0.067
π (C12=C14)	1.66236	π* (C7=C9)	0.37839	19.75	0.28	0.067
		π* (C8=C10)	0.31915	20.34	0.28	0.068
π (C18=C20)	1.64053	π* (C19=C21)	0.32471	19.08	0.28	0.065
		π* (C23=C25)	0.34146	21.90	0.27	0.070
π (C19=C21)	1.67604	π* (C18=C20)	0.36269	20.25	0.28	0.068
		π* (C23=C25)	0.34146	19.60	0.28	0.066
π (C23=C25)	1.66737	π* (C18=C20)	0.36269	19.17	0.29	0.066
		π* (C19=C21)	0.32471	20.51	0.28	0.068
π (C38=C38)	1.66452	π* (C37=C39)	0.32345	19.48	0.28	0.066

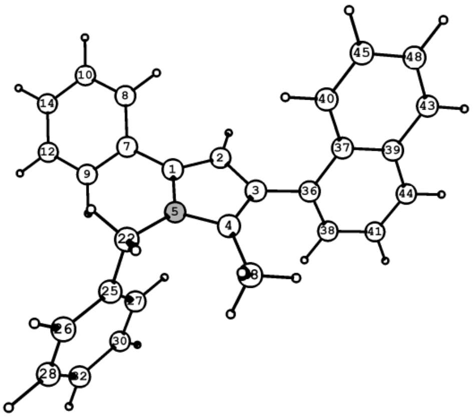
		π* (C41=C43)	0.32301	20.54	0.28	0.068
π (C37=C39)	1.67838	π* (C36=C38)	0.34260	20.91	0.28	0.069
		π* (C41=C43)	0.32301	19.35	0.28	0.066
π (C41=C43)	1.66912	π* (C36=C38)	0.34260	19.56	0.28	0.066
		π* (C37=C39)	0.32345	20.82	0.28	0.068
LP (N5)	1.58382	π* (C1=C2)	0.35702	32.98	0.30	0.090
		π* (C3=C4)	0.36809	34.66	0.30	0.092

[a] ED is the electron occupancy

[b] E (2) means energy of hyper conjugative interaction (stabilization energy).

[c] Energy difference between donor and acceptor i and j NBO orbitals.

[d] F (i, j) is the Fork matrix element between i and j NBO orbitals.



Scheme S3. Atom numbering scheme adopted for diaryl-pyrrole **1b**.

Table S2- Second-order perturbation theory analysis of Fock matrix in NBO analysis for selected orbital pairs of the diaryl-pyrrole **1b**.

Donor (i)	**ED/e** [a]	**Acceptor (j)**	**ED/e** [a]	**E(2)** [b] **(kcal mol^{-1})**	**E(j)-E(i)** [c] **(a.u.)**	**F(i,j)** [d] **(a.u.)**
π (C1=C2)	1.81597	π* (C3=C4)	0.35998	17.46	0.30	0.067
π (C3=C4)	1.79825	π* (C1=C2)	0.35846	17.67	0.29	0.067
π (C7=C9)	1.64149	π* (C1=C2)	0.35846	10.17	0.29	0.049
		π* (C8=C10)	0.31855	18.96	0.28	0.066
		π* (C12=C14)	0.33807	21.13	0.28	0.069
π (C8=C10)	1.67570	π* (C7=C9)	0.37893	19.77	0.28	0.068
		π* (C12=C14)	0.33807	19.60	0.28	0.067
π (C12=C14)	1.66230	π* (C7=C9)	0.37893	19.75	0.28	0.067
		π* (C8=C10)	0.31855	20.33	0.28	0.068
π (C25=C27)	1.66485	π* (C26=C28)	0.32314	19.46	0.28	0.066
		π* (C30=C32)	0.32285	20.53	0.28	0.068
π (C26=C28)	1.67826	π* (C25=C27)	0.34283	20.92	0.28	0.069
		π* (C30=C32)	0.32285	19.35	0.28	0.066
π (C30=C32)	1.66910	π* (C25=C27)	0.34283	19.57	0.28	0.066
		π* (C26=C28)	0.32314	20.81	0.28	0.068

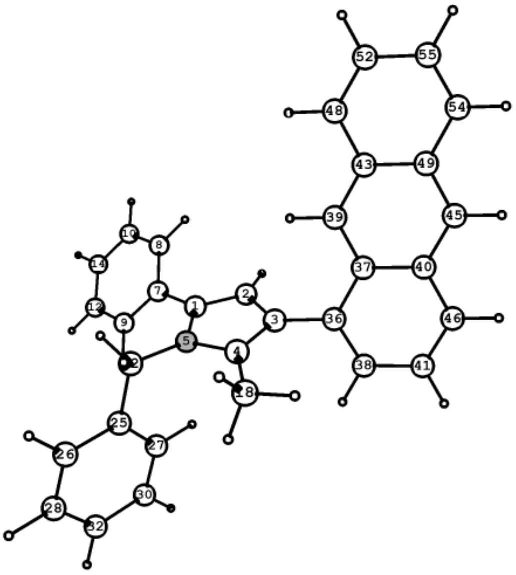
π (C36=C38)	1.72556	π* (C37=C39)	0.46037	15.32	0.28	0.062
		π* (C41=C44)	0.25957	18.42	0.29	0.065
π (C37=C39)	1.53558	π* (C36=C38)	0.27549	16.82	0.28	0.064
		π* (C40=C45)	0.25283	16.88	0.27	0.064
		π* (C41=C44)	0.46037	16.30	0.27	0.063
		π* (C43=C48)	0.25594	16.47	0.27	0.063
π (C40=C45)	1.73954	π* (C37=C39)	0.46037	15.88	0.29	0.064
		π* (C43=C48)	0.25594	17.75	0.29	0.064
π (C41=C44)	1.74609	π* (C36=C38)	0.27549	16.67	0.3	0.063
		π* (C37=C39)	0.46037	16.15	0.29	0.065
π (C43=C48)	1.74594	π* (C37=C39)	0.46037	16.03	0.29	0.064
		π* (C40=C45)	0.25283	17.09	0.30	0.064
LP (N5)	1.58550	π* (C1=C2)	0.35846	33.07	0.30	0.089
		π* (C3=C4)	0.35998	34.82	0.30	0.092

[a] ED is the electron occupancy

[b] E (2) means energy of hyper conjugative interaction (stabilization energy).

[c] Energy difference between donor and acceptor i and j NBO orbitals.

[d] F (i, j) is the Fork matrix element between i and j NBO orbitals.



Scheme S4. Atom numbering scheme adopted for diaryl-pyrrole **1c**.

Table S3- Second-order perturbation theory analysis of Fock matrix in NBO analysis for selected orbital pairs of the diaryl-pyrrole **1c**.

Donor (i)	**ED/e** [a]	**Acceptor (j)**	**ED/e** [a]	**E(2)** [b] **(kcal mol^{-1})**	**E(j)-E(i)** [c] **(a.u.)**	**F(i,j)** [d] **(a.u.)**
π (C1=C2)	1.96996	π* (C3=C4)	0.35995	17.45	0.30	0.067
π (C3=C4)	1.79827	π* (C1=C2)	0.35762	17.64	0.29	0.067
π (C7=C9)	1.64144	π* (C1=C2)	0.35762	10.21	0.29	0.049
		π* (C8=C10)	0.31879	18.97	0.28	0.066

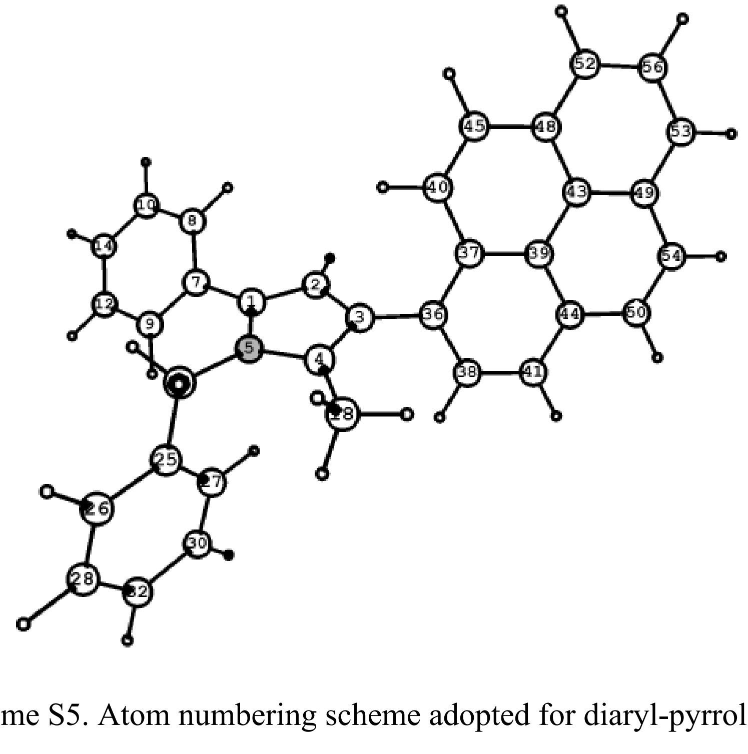
		π* (C12=C14)	0.33797	21.11	0.28	0.069
π (C8=C10)	1.67574	π* (C7=C9)	0.37888	19.78	0.28	0.068
		π* (C12=C14)	0.33797	19.59	0.28	0.067
π (C12=C14)	1.66207	π* (C7=C9)	0.37888	19.77	0.28	0.067
		π* (C8=C10)	0.31879	20.34	0.28	0.068
π (C25=C27)	1.66493	π* (C26=C28)	0.32306	19.44	0.28	0.066
		π* (C30=C32)	0.32283	20.54	0.28	0.068
π (C26=C28)	1.67807	π* (C25=C27)	0.34312	20.93	0.28	0.069
		π* (C30=C32)	0.32283	19.36	0.28	0.066
π (C30=C32)	1.66894	π* (C25=C27)	0.34312	19.58	0.28	0.066
		π* (C26=C28)	0.32306	20.82	0.28	0.068
π (C36=C38)	1.75412	π* (C41=C46)	0.23003	17.29	0.29	0.064
π (C40=C45)	1.62414	π* (C41=C46)	0.23003	18.01	0.29	0.067
π (C41=C46)	1.77454	π* (C36=C38)	0.24622	15.62	0.30	0.062
		π* (C40=C45)	0.37344	17.01	0.29	0.066
π (C48=C52)	1.77501	π* (C39=C43)	0.37205	16.46	0.30	0.065
		π* (C54=C55)	0.22414	16.34	0.30	0.062
π (C54=C55)	1.77624	LP* (C49)	0.99964	34.63	0.16	0.084
		π* (C48=C52)	0.22425	16.11	0.30	0.062
LP (N5)	1.58569	π* (C1=C2)	0.35762	32.94	0.30	0.089
		π* (C3=C4)	0.35995	34.89	0.30	0.093

[a] ED is the electron occupancy

[b] E (2) means energy of hyper conjugative interaction (stabilization energy).

[c] Energy difference between donor and acceptor i and j NBO orbitals.

[d] F (i, j) is the Fork matrix element between i and j NBO orbitals.



Scheme S5. Atom numbering scheme adopted for diaryl-pyrrole **1d**.

Table S4- Second-order perturbation theory analysis of Fock matrix in NBO analysis for selected orbital pairs of the diaryl-pyrrole **1d**.

Donor (i)	ED/e [a]	Acceptor (j)	ED/e [a]	E(2) [b] (kcal mol^{-1})	E(j)-E(i) [c] (a.u.)	F(i,j) [d] (a.u.)
π (C1=C2)	1.81634	π* (C3=C4)	0.36328	17.43	0.30	0.067
π (C3=C4)	1.79500	π* (C1=C2)	0.35761	17.66	0.29	0.067
π (C7=C9)	1.64178	π* (C1=C2)	0.35761	10.06	0.29	0.048
π (C7=C9)		π* (C8=C10)	0.31877	18.99	0.28	0.066
π (C7=C9)		π* (C12=C14)	0.33781	21.09	0.28	0.069
π (C8=C10)	1.67513	π* (C7=C9)	0.37864	19.79	0.28	0.068
π (C8=C10)		π* (C12=C14)	0.33781	19.63	0.28	0.067
π (C12=C14)	1.66176	π* (C7=C9)	0.37864	19.80	0.28	0.067
π (C12=C14)		π* (C8=C10)	0.31877	20.33	0.28	0.068
π (C25=C27)	1.66525	π* (C26=C28)	0.32294	19.44	0.28	0.066
π (C25=C27)		π* (C30=C32)	0.32262	20.51	0.28	0.068
π (C26=C28)	1.67805	π* (C25=C27)	0.34320	20.93	0.28	0.069
π (C26=C28)		π* (C30=C32)	0.32262	19.36	0.28	0.066
π (C30=C32)	1.66888	π* (C25=C27)	0.34320	19.59	0.28	0.066
π (C30=C32)		π* (C26=C28)	0.32294	20.81	0.28	0.068
π (C36=C38)	1.64043	π* (C37=C39)	0.45943	17.98	0.28	0.065
π (C36=C38)		π* (C41=C44)	0.39444	20.65	0.28	0.068
π (C37=C39)	1.53372	π* (C36=C38)	0.36078	19.65	0.27	0.067
π (C37=C39)		π* (C40=C45)	0.19118	14.38	0.28	0.061
π (C37=C39)		π* (C41=C44)	0.39444	18.61	0.27	0.064
π (C37=C39)		π* (C43=C48)	0.46157	18.94	0.27	0.064
π (C40=C45)	1.80077	π* (C37=C39)	0.45943	13.27	0.30	0.06
π (C40=C45)		π* (C43=C48)	0.46157	13.78	0.30	0.061
π (C41=C44)	1.60946	π* (C36=C38)	0.36078	20.51	0.28	0.068
π (C41=C44)		π* (C37=C39)	0.45943	18.10	0.28	0.065
π (C41=C44)		π* (C50=C54)	0.19472	16.98	0.29	0.066
π (C43=C48)	1.52834	π* (C37=C39)	0.45943	19.15	0.27	0.065
π (C43=C48)		π* (C40=C45)	0.19118	13.83	0.28	0.06
π (C43=C48)		π* (C49=C53)	0.38878	18.99	0.27	0.065
π (C43=C48)		π* (C52=C56)	0.33843	18.96	0.27	0.066
π (C49=C53)	1.61474	π* (C43=C48)	0.46157	17.52	0.28	0.064
π (C49=C53)		π* (C50=C54)	0.19472	16.65	0.29	0.065
π (C49=C53)		π* (C52=C56)	0.33843	20.94	0.28	0.069
π (C50=C54)	1.80630	π* (C41=C44)	0.39444	15.46	0.30	0.064
π (C50=C54)		π* (C49=C53)	0.38878	15.74	0.30	0.064
π (C52=C56)	1.66813	π* (C43=C48)	0.46157	18.55	0.29	0.067
π (C52=C56)		π* (C49=C53)	0.38878	18.74	0.28	0.066
LP (N5)	1.58354	π* (C1=C2)	0.35761	33.07	0.30	0.090
LP (N5)		π* (C3=C4)	0.36328	35.08	0.30	0.093

[a] ED is the electron occupancy

[b] E (2) means energy of hyper conjugative interaction (stabilization energy).

[c] Energy difference between donor and acceptor i and j NBO orbitals.

[d] F (i, j) is the Fork matrix element between i and j NBO orbitals.

5. References

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