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Prominent Bathochromic Shift Effect of Indole-Containing Diarylethene Derivatives

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The potential implication of photochromic materials with absorption and reactivity in the near-infrared region is far-reaching. In this work, three novel bisindole-containing diarylethene derivatives **1o–3o** have been successfully synthesized and their photochromic behaviours exhibit strong bathochromic shift effect compared with bisbenzothiophene diarylethene **4o**. These new bisindole-diarylethene compounds **1o–3o** are highly sensitive to photo-stimuli both in solution and in poly(methyl methacrylate) films. Besides, **1o–3o** exhibit excellent reversible fluorescence switching behavior modulated by optical stimuli.

1. Introduction

Photochromic materials have attracted a great deal of interest because their photoisomerization can be used to develop photochemically controllable materials for novel photoswitching devices and optical data storage.[1] Photochromic compounds with absorption and reactivity in the near-infrared (NIR) region can enhance the semiconductor diode laser susceptibility for applications in optical memory storage.[2] Among various photochromic compounds, diarylethene derivatives (DAEs) are the most promising optically responsive compounds in photochemistry and materials science owing to their reversible transformations between ring-open and ring-closed conformations that have markedly different optical and electronic properties.[3] To achieve NIR-absorption in DAEs, one commonly used method is to augment the π-conjugation of the thiophene moiety. But, this approach often requires laborious syntheses and suffers from the convergence limit of the bathochromic shift effect.[4] Therefore, different attempts have been made to construct diarylethene derivatives with NIR absorptions. Yam and co-workers reported an innovative way of achieving NIR photochromic behaviour through metal-coordination-assisted planarization of the extended π-conjugated system in dithienylethene.[5] Recently, Tian and coworkers constructed two NIR photochromic systems by introducing electron-donating (D) and electron-accepting moieties (A) to DAEs, whose fluorescence performance can be modulated by cyanide anion.[6] Diarylethenes containing thiophene moieties have been intensively investigated.[7] Compared with thiophene, indole ring has higher electron density that may have potential influence on the photochromic performance of DAEs. However, bisindole-containing

diarylethenes have rarely been exploited to construct NIR photochromic systems so far.

Herein, we described the design and syntheses of three bisindole diarylperfluorocyclopentenes **1o–3o** as well as the reference compound bisbenzothiophene diarylethene **4o** (Scheme 1), and investigated their photochromic behavior and photophysical properties. The compounds **1o–3o** form molecular switches that undergo light-induced cyclization and decyclization reactions. We introduced perfluorocyclopentene to DAEs **1o–3o** as the central ethene linker because of its resistance to fatigue.[8] Interestingly, **1o–3o** exhibited prominent bathochromic shift effect to the NIR region compared with the reference compound **4o**.
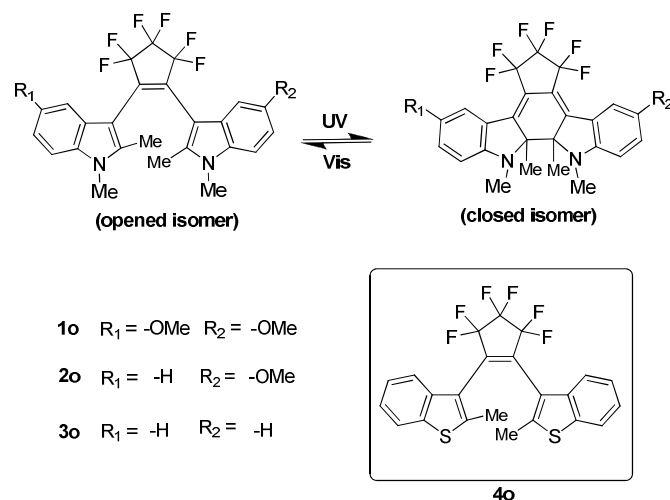

Scheme 1. Photoisomerization of **1o–3o** and the reference compound **4o**.

2. Results and Discussion

Synthesis

The syntheses of photochromic diarylethenes **1o**–**3o** are illustrated in Scheme 2. The open diarylehene **1o** and open diarylehene **3o** were prepared in 52–55% yield by lithiation of 3-bromo-5-methoxy-1,2-dimethyl-1H-indole (**5**) and 3-bromo-1,2-dimethyl-1H-indole (**6**) followed by the addition of 0.5 equivalent octafluorocyclopentene.[9] The open diarylehene **2o** was synthesized by lithiation of 3-bromo-1,2-dimethyl-1H-indole (**6**) followed by the addition of 5-methoxy-1,2-dimethyl-3-(perfluorocyclopent-1-enyl)-1H-indole (**7**). The compounds were characterised by NMR spectroscopy, mass spectroscopy, and X-ray crystallographic analysis. (see Supporting Information Figures S1–S9).
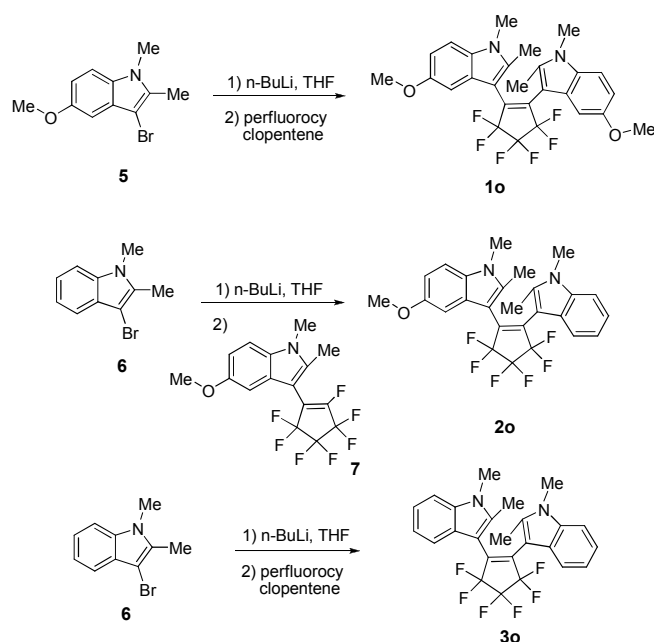
Scheme 2. Syntheses of compounds **1o**–**3o**.

X-ray crystallographic study

The single crystals of **1o** were acquired by slow evaporation from an ethyl acetate/hexane (1:1, v/v) solution at room temperature for a week. Single-crystal X-ray diffraction measurements reveal that **1o** crystallize in the monoclinic space group $P2_1/n$. The X-ray crystallographic data are listed in Table S1. As shown in Figure 1, the structure of **1o** exclusively adopts the antiparallel conformations, which are in sharp contrast to the solution-phase behavior, where the antiparallel and parallel conformers coexist.[8] The distance between the photocyclizing carbon atoms C8 and C24 is 3.768 Å.

The crystals of **1o** would show photochromic effect upon irradiation with UV light because photochromic reactivity usually appears when the distance between the reactive C atoms

is less than 4.2 Å and the molecule is fixed in an antiparallel mode.[10] Torsion angles between indole and hexafluorocyclopentene rings are -47.3° (C6-C7-C12-C13) and -56.2° (C15-C16-C17-C18). Interestingly, **1o** also shows photochromic reactivity in the crystalline state. Upon irradiation with 365 nm light, the pale crystals of **1o** turned blue, and the blue color faded after irradiation with visible light (Figure 2).
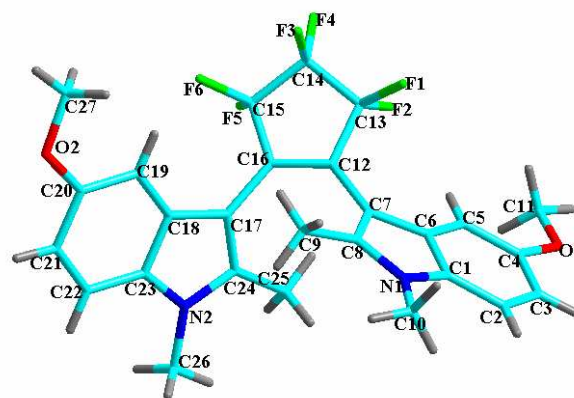
Figure 1 . Crystal structure of **1o**.

Molecular packing arrangements of **1o** were shown in Figure 3. In the crystal, the intermolecular C-H···F and C-H···O interactions are clearly noticed.[11] Fluorine atoms F2 and F3 of the hexafluorocyclopentene ring serve as the acceptors for hydrogen atoms H5 and H2 of the indole ring of the adjacent molecule, respectively. Oxygen atom O1 serves as acceptor for hydrogen atom H3 of the neighbouring molecule. Consequently, a 3D supramolecular network was formed via hydrogen-bonding interactions in **1o** (C(2)–H(2)···F(3), 3.467(2) Å, 173°; C(3)–H(3)···O(1), 3.403(2) Å, 154°; C(5)–H(5)···F(2), 3.083(2) Å, 132°).

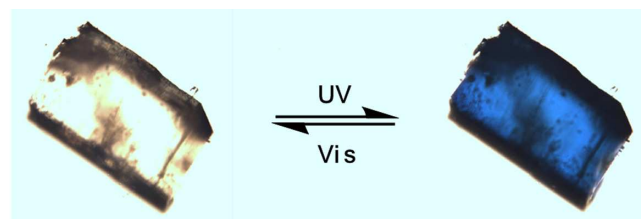Figure 2 Color changes of a single crystal of **1o** upon alternating irradiation at UV/Vis.

Photochromic Behaviour

The backbones of DAEs **1o**–**3o** could switch between colorless open forms and colored closed forms by alternated irradiation with UV and visible light. The spectral changes of bisindole-containing **1o**–**3o** and reference compound **4o** in hexane exposed to UV light are shown in Figures S10 and
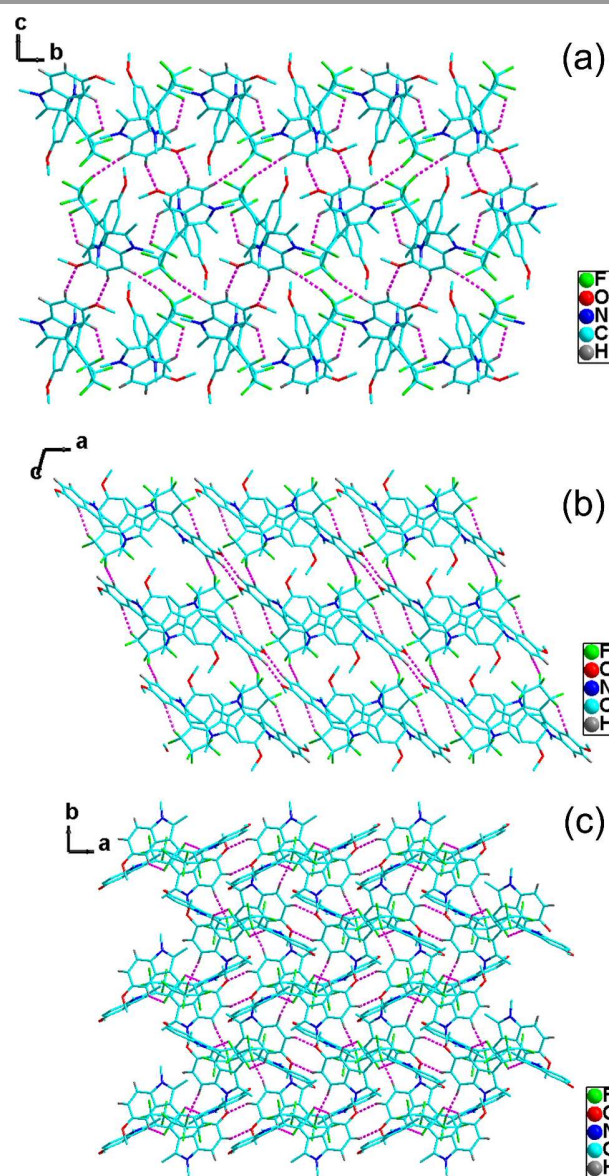
Figure 3 Molecular packing diagrams of **1o**.

The photochromic properties of DAEs **1o**–**4o** in toluene are similar to those in hexane (Figure 4). Upon 365 nm UV light irradiation, the spectral changes of **1o**–**4o** in toluene are shown in Figure S4. The absorption showed evident bathochromic shift effect with the increase in the polarity of solvents. The photo-generated closed-ring isomers **1c**–**4c** have their absorption maxima at 638, 620, 593 and 523 nm, respectively. As shown in Table 1, the absorption maxima of closed-ring isomers **1c**–**4c** underwent an obvious solvent-induced red shift of 26, 26, 21, and 9 nm, respectively. Moreover, the thermal stability of closed-ring isomer **1c** was investigated by UV/vis spectroscopy at an elevated temperature of 45°C. The signal of thermal ring opening was hardly observed for at least 270 min upon monitoring at 638, 466 and 350 nm (Figure 5). We also examined the fatigue resistance properties of **1o**–**3o** upon alternating UV and visible-light irradiation. As shown in Figure S13, the cycles could be repeated many times without any significant degradation in toluene. The quantum yields of **1o**–**3o** are summarized in Table S3 (Supporting Information). The photocyclization quantum yields (Φ_{o-c}) for active conformers were determined to be 0.28 for **1o**, 0.20 for **2o** and 0.25 for **3o**.

Table 1. The UV-vis absorption maxima of compounds **1o**–**4o** in hexane and toluene before and after irradiation with 365 nm light at 25 °C (0–2 min).

compounds	Hexane		Toluene	
	λ_{max} (open)	λ_{max} (closed)	λ_{max} (open)	λ_{max} (closed)
1o	277 nm	612 nm	282 nm	638 nm
2o	280 nm	594 nm	289 nm	620 nm
3o	279 nm	572 nm	286 nm	593 nm
4o	266 nm	514 nm	281 nm	523 nm
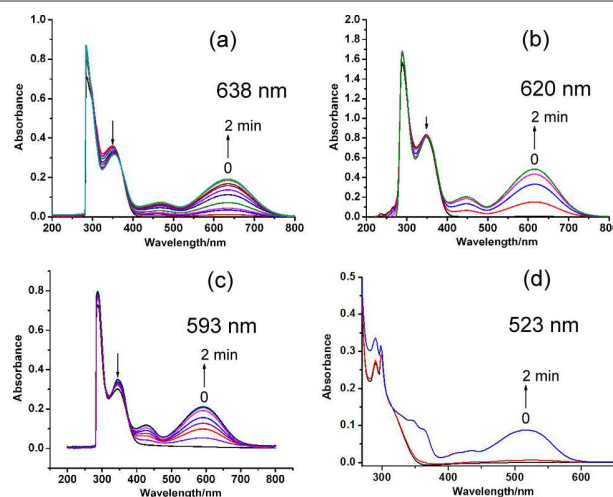
Figure 4 UV-vis spectral changes of (a) **1o**, (b) **2o,** (c) **3o** and (d) **4o** upon UV light (365 nm) irradiation in toluene at 25 °C (0–2 min).

Table 1. Upon irradiation with 365 nm UV-light, the initially colorless solutions of compounds **1o**–**4o** display a strong coloration and the photo-generated closed-ring isomers have their absorption maxima at 612, 594, 572 and 514 nm, respectively. Compared with reference compound **4o**, compounds **1o**–**3o** showed strong bathochromic shift effect (~98 nm for **1o,** ~80 nm for **2o** and ~58 nm for **3o**) upon UV light irradiation. Once switched to visible light irradiation, the bluish color disappeared and the absorption peaks of the open-ring forms were restored. The stronger bathochromic shift of **1c** compared with **2c** and **3c** is probably due to substituent effects. This observation confirmed that indole and its derivatives can play a crucial role in constructing NIR-responsive photochromic materials.

In addition, **1o**–**3o** are highly sensitive and responsive to photo-stimuli in poly(methyl methacrylate) (PMMA) film (Figure S11). Irradiation with UV-light triggers the emergence

of a new absorption band in the visible light range, with **1c**, **2c** and **3c** having their maxima at 649, 628 and 600 nm, respectively. The absorption maxima of closed-ring isomers **1c**–**3c** underwent an obvious red shift of 11, 8 and 7 ppm compared with the absorption maxima of these compounds in toluene. This observation further confirmed that altering the electronic properties of the heteroaryl moieties is an efficient approach to fine-tune the spectral profiles of these photochromic materials.[12]
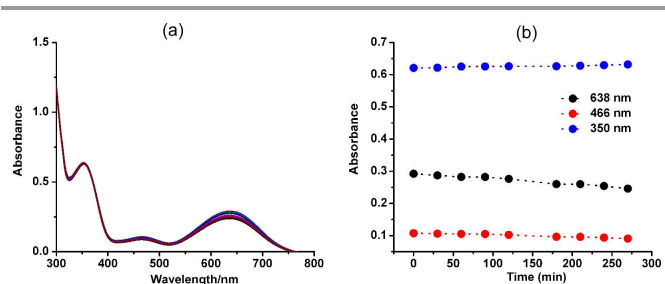

Figure 5 (a) UV-vis spectra of a mixture of **1o** and **1c** (obtained by UV irradiation of **1o** in toluene) before and after heating at 45 °C.(b) Absorbance changes of the **1o/1c** mixture monitored at 638, 466, and 350 nm
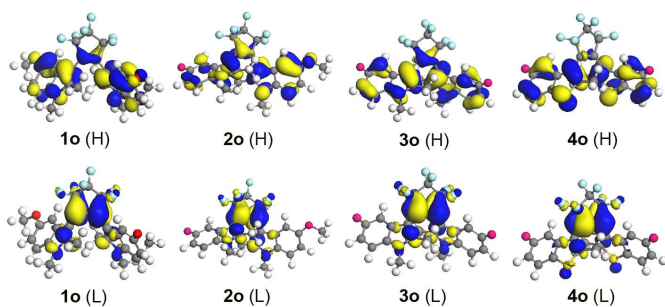

Figure 6 Optimized molecular structures with HOMO (H) / LUMO (L) electron density distributions of **1o**, **2o**, **3o** and **4o** respectively.

Table 2. HOMO, LUMO and HOMO-LUMO energy levels for **1o**, **2o**, **3o** and **4o** respectively.

	1o	**2o**	**3o**	**4o**
HOMO (eV)	-4.618	-4.718	-4.838	-5.536
LUMO (eV)	-2.142	-2.196	-2.265	-2.265
HOMO-LUMO energy level (eV)	2.476	2.522	2.573	3.271

In order to clarify the origin of the bathochromic shift effect of the bisindole-containing diarylethene derivatives, we performed density functional theory (DFT) calculations of the HOMO/LUMO electron density distributions of **1o**, **2o**, **3o** and **4o** respectively (Figure 6). Their HOMO/LUMO and HOMO-LUMO energy levels are compared in Table 2. The HOMO-LUMO energy levels considerably increase from **1o** to **4o**, which means that the electronic transitions in **1o** are the easiest while those in **4o** are the most difficult. This result is supportive of the bathochromic shift effect observed in the present work.

The bisindole-containing DAEs **1o**–**3o** also displayed excellent fluorescence performance. The quantum yields of open-ring isomers **1o**–**3o** were 0.33, 0.28 and 0.10 in toluene,

respectively. The fluorescence of DAEs **1o**–**3o** can also be modulated by the photochromism. Upon excitation at the isosbestic point of 371 nm, **1o** exhibits an intense fluorescence at ca. 455 nm (Figure S12a). Upon irradiation at UV (365 nm), an obvious fluorescence quenching was observed on account of the resulting closed form (**1c**). When the photostationary state is reached, the fluorescence intensity of **1o** decreased by about 90%.

Irradiation of **2o** using the 365 nm UV light in a dark room converts the open form of **2o** to the closed form with the maximum fluorescence intensity decreasing by ~88% (Figure S12b). On the other hand, as seen from Figure S12c, upon excitation at the isosbestic point of 370 nm, **3o** exhibits excellent fluorescence with an intense fluorescence at ca. 454 nm. When the open form of **3** was exposed to 365 nm UV light, photocyclization took place, and the emission intensity at ca. 455 nm was decreased and almost completely quenched. However, when the closed forms of DAEs **1o**–**3o** were exposed to visible light, the emission could be recovered without any significant degradation in fluorescence intensity. These observations jointly indicate **1o**–**3o** caused remarkable fluorescence changes, allowing them to behave as reversible optical molecular switches.

3. Conclusions

In summary, we have designed and synthesized three bisindole diarylethene derivatives **1o**–**3o** and their photochromic behaviors show prominent red shift to the NIR region compared with the reference compound **4o**. The photophysical and photochromic properties of **1o**–**3o** were comprehensively investigated by UV/vis, fluorescence spectra and X-ray crystallographic analysis. Compared with **2o** and **3o**, **1o** exhibits stronger red shift both in solution and in PMMA under UV irradiation probably due to the substituent effect. Moreover, **1o**–**3o** undergo light-induced cyclization and decylization reactions and show excellent photochromic properties accompanied with efficient quenching of fluorescence emission by the closed form of the diarylethene moiety. These features allow them to behave as reversible optical molecular switches. We believe the results presented here will provide a new perspective for the design of NIR-sensitive molecular machines and smart materials.

4. Experimental

Instrumentation

All the commercial reagents unless otherwise annotated were purchased from Sigma Aldrich, Alfa Aesar and were used without further purification. 3,3'-(perfluorocyclopent-1-ene-1,2-diyl)bis(2-methylbenzo[b]thiophene) (**4o**),[13] 3-bromo-5-methoxy-1,2-dimethyl-1H-indole (**5**),[14] 3-bromo-1,2-dimethyl-1H-indole (**6**)[14] and 5-methoxy-1,2-dimethyl-3-(perfluorocyclopent-1-enyl)-1H-indole (**7**)[8] were prepared according to the literatures procedure. NMR spectra were recorded on a Varian Mercury VX400 instrument. The optical

switch experiments were carried out using a photochemical reaction apparatus with a 500W Hg lamp. UV/Vis spectra were recorded with a Shimadzu UV-3600 spectrophotometer equipped with a PTC-348WI temperature controller. Steady-state fluorescence spectra were recorded in a conventional quartz cell (light path 10 mm) on a Varian Cary Eclipse equipped with a Varian Cary single-cell Peltier accessory to control the temperature. The method preparation of PMMA Film: photochromic materials **1o–3o** was dissolved in 3 ml of chloroform. The solution was filtered using membranes and added PMMA in the solution stirring until the PMMA was resolved. The solution was spin-coated on a glass substrate with a spin rate of 2000 rpm. The coated film was dried in a vacuum oven to give transparent and homogeneous film.

Preparation of Compound 1o:

n-Butyllithium (2.4 M in hexane, 15.6 mmol, 6.5 mL) was added dropwise to a stirred solution of 3-bromo-5-methoxy-1,2-dimethyl-1H-indole **5** (3.04 g, 12 mmol) in 100 mL of THF at −78 °C under a nitrogen atmosphere. After 60 min, a solution of compound perfluorocylcopentene (1.27 g, 6 mmol) in 20 mL of THF was added dropwise to the reaction mixture. The reaction mixture was stirred for 1 hour at −78 °C, then allowed to warm up to room temperature, and stirred for additional 16 h. After addition of 100 mL of water, THF was removed under reduced pressure, and the residue was extracted with CH_2Cl_2 (3 × 30 mL). The combined organic phases were dried over $MgSO_4$, filtered and evaporated in vacuo and chromatographed with silica gel. Elution with a 1:15 acetic ether/hexane mixture afforded **1o** as yellow crystals (1.63 g, 52%). Mp: 244-245 °C; ^{1}H NMR (400 MHz $CDCl_3$) δ 6.97-6.95 (d, J = 9.5 Hz, 2H) 6.88 (s, 2H) 6.69-6.67 (d, J = 8.2 Hz, 2H) 3.51 (s, 6H) 3.37 (s, 6H) 1.88 (s, 6H); ^{13}C NMR (100 MHz $CDCl_3$) δ 154.7, 138.2, 132.0, 126.3, 111.5, 109.6, 101.6, 101.5, 101.5, 55.5, 29.9, 11.6; HRMS (ESI) m/z [M+H]$^+$ calcd for $C_{27}H_{25}F_6N_2O_2^+$ 523.1820, found 523.1809. IR (KBr) ν: 3458, 2933,,2832, 1620, 1488, 1450, 1299, 1273, 1217, 1182, 1159, 1119, 1088, 1044, 1028, 977, 868, 839, 802, 794, 750, 706, 559, 435 cm^{-1}.

Preparation of Compound 2o:

n-Butyllithium (2.4 M in hexane, 15.6 mmol, 6.5 mL) was added dropwise to a stirred solution of 3-bromo-1,2-dimethyl-1H-indole **6** (2.69 g, 12 mmol) in 100 mL of THF at −95 °C under a nitrogen atmosphere. After 60 min, a solution of compound 5-methoxy-1,2-dimethyl-3-(perfluorocyclopent-1-enyl)-1H-Indole **7** (4.38 g, 12 mmol) in 20 mL of THF was added dropwise to the reaction mixture. The reaction mixture was stirred for 1 hour at −78 °C, then allowed to warm up to room temperature, and stirred for additional 16 h. After addition of 100 mL of water, THF was removed under reduced pressure, and the residue was extracted with CH_2Cl_2 (3 × 30 mL). The combined organic phases were dried over $MgSO_4$, filtered and evaporated in vacuo and chromatographed with silica gel. Elution with a 1:18 acetic ether/hexane mixture afforded **2o** as yellow crystals (2.95 g, 50%). Mp: 237-238°C; ^{1}H NMR (400 MHz $CDCl_3$) δ: 7.71-7.69 (d, J = 7.7 Hz, 1H)

7.15-7.14(d, J = 3.8 Hz, 1H) 7.11-7.08 (dd, J_{1-2} = 4.4 Hz, J_{1-3} = 8.0 Hz, 1H) 7.02-6.99 (d, J = 8.8 Hz, 1H) 6.83 (s, 1H) 6.73-6.71 (d, J = 8.7 Hz, 1H) 3.49 (s, 3H) 3.44 (s, 3H) 3.41 (s, 3H) 2.01 (s, 3H) 1.84 (s, 3H); ^{13}C NMR (100 MHz $CDCl_3$) δ: 247.9, 154.6, 138.1, 137.9, 136.9, 131.9, 126.2, 126.1, 121.6, 120.6, 119.9, 119.6, 119.6, 111.5, 109.6, 108.9, 101.7, 101.2, 55.5, 29.8, 29.7, 11.7, 11.3; HRMS (ESI) m/z [M+H]$^+$ calcd for $C_{26}H_{23}F_6N_2O^+$ 493.1715, found 493.1700. IR (KBr) ν: 3686, 2948, 1619, 1539, 1488, 1438, 1338, 1272, 1218, 1181, 1159, 1119, 1042, 975, 839, 813, 798, 764, 744, 556 cm^{-1}.

Preparation of Compound 3o[9]:

n-Butyllithium (2.4 M in hexane, 15.6 mmol, 6.5 mL) was added dropwise to a stirred solution of 3-bromo-1,2-dimethyl-1H-indole **6** (2.69 g, 12 mmol) in 100 mL of THF at −78 °C under a nitrogen atmosphere. After 60 min, a solution of compound perfluorocylcopentene (1.27 g, 6 mmol) in 20 mL of THF was added dropwise to the reaction mixture. The reaction mixture was stirred for 1 hour at −78 °C, then allowed to warm up to room temperature, and stirred for additional 16 h. After addition of 100 mL of water, THF was removed under reduced pressure, and the residue was extracted with CH_2Cl_2 (3 × 30 mL). The combined organic phases were dried over $MgSO_4$, filtered and evaporated in vacuo and chromatographed with silica gel. Elution with a 1:15 acetic ether/hexane mixture afforded **3o** as yellow crystals (1.52 g, 55%). Mp: 222-223 °C; ^{1}H NMR (400 MHz $CDCl_3$) δ: 7.64-7.62(d, J = 7.7 Hz, 2H) 7.19-7.14(dd, J_{1-2} = 7.5 Hz, J_{1-3} = 13.8 Hz, 4H) 7.11-7.09 (d, J=7.3 Hz, 2H) 3.49 (s, 6H) 1.89 (s, 3H); ^{13}C NMR (100 MHz $CDCl_3$) δ: 136.6, 135.787, 125.1, 120.5, 119.5, 118.5, 118.5, 118.4, 107.9, 100.3, 28.8, 10.4; HRMS (ESI) m/z [M+H]$^+$ calcd for $C_{25}H_{21}F_6N_2^+$ 463.1609, found 463.1594. IR (KBr) ν: 3052, 2918, 1542, 1475, 1329, 1269, 1233, 1179, 1117, 1087, 1040, 1001, 969, 849, 822, 802, 743, 554 cm^{-1}.

Molecular Orbital Calculation Method

In this study, we use spin-unrestricted density functional theory (DFT) method for the molecular orbital calculations. Simulations are carried out through an effective core potentials method within the Perdew, Burke and Ernzerhof (PBE) of general gradient approximations (GGA) exchange-correction functional approximation as implemented in the DMol3 program package in the Materials Studio of Accelrys Inc. The basis set is chosen as DND. The real-space global orbital cutoff radius quality is set as high as fine. Fully relaxed geometries are obtained by optimizing all atomic positions until the energy convergence tolerance, force convergence tolerance and displacement convergence tolerance are less than $1×10^{-5}$ Ha, 0.002 Ha and 0.005 Å, respectively.

Notes and references

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