Tetrahedron 66 (2010) 9641–9649

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Synthesis and computational studies of diphenylamine donor-carbazole linker-based donor–acceptor compounds

Krishna Panthi[a], Patrick Z. El-Khoury[a,b], Alexander N. Tarnovsky[a], Thomas H. Kinstle[a,*]

[a] Department of Chemistry and Center for Photochemical Sciences, Bowling Green State University, Bowling Green, OH 43403, USA
[b] Department of Chemistry, University of California, Irvine, CA, USA

ARTICLE INFO

Article history:
Received 16 August 2010
Received in revised form 15 October 2010
Accepted 18 October 2010
Available online 8 November 2010

Keywords:
Diphenylamine donor-carbazole linker
Phenylethynyl extender
Electronic transitions
Control DD compounds
TD DFT calculations

ABSTRACT

The design, synthesis, and electronic spectra of a novel series of organic diphenylamine donor-carbazole linker-based donor–acceptor compounds are reported. The low-lying electronic transitions in these compounds are investigated using a combination of conventional steady-state absorption spectroscopy and tools of computational photochemistry. The electronic transitions were found to depend both on the nature of the acceptor moiety and the presence/absence of a carbazole linker, not affected by the presence of the trifluoromethlyphenyl group in all the reported DA compounds.

1. Introduction

Linear π-conjugated systems constitute one of the most extensively studied classes of organic compounds. Research efforts in this field cover a broad spectrum of topics ranging from purely fundamental investigations to exploring the potential applications of individual compounds and their ensembles in nanoelectronics and solar energy conversion.[1]

In this regard, the electronic and optical properties of conjugated small molecules have attracted much attention in the past few decades.[2,3] Specifically, the molecular architecture and strong absorption and emission properties of donor–acceptor (DA) complexes separated by different lengths of linkers have rendered these molecules useful as emitters in organic light-emitting diodes (OLEDs)[4,5] and sensitizers in dye-sensitized solar cells (DSSCs).[6,7] Carbazole- and diphenylamine-based DA compounds have recently found use as wide band gap energy transfer materials as well as promising applications in the area of hole-transporting.[8,9] To date, a number of derivatized carbazole- and diphenylamine-based DA compounds have been designed, synthesized, and characterized because of their tunable intramolecular charge transfer properties. It has been found that the molecular and optical properties of carbazole-based compounds can be controlled by modifying the 2-, 3-, 6-, 7-, and 9-positions of the carbazole.[10,11] There are only a few examples in the literature of DA type compounds in which triphenylamine was linked to the 3-position of a carbazole[12] and/or diphenylamine was linked to a fluorene.[13] However, there are no reported compounds in which diphenylamine or triphenylamine donors are linked to the 2-position of the linker carbazole to form D–π-A molecules. Previous molecular designs have been mostly focused on networking through the 3-, 6-positions,[14–16] and only a handful of examples have the conjugation through the 2-, 7-,[17–20] and 9-positions.[21,22]

This work presents the synthesis and characterization of a novel series of diphenylamine donor-based compounds (**1**–**6**) having 2-,7-carbazole linkers all with/without phenylethynyl extenders attached to a terminal acceptor or donor group, Fig. 1. Compounds **1** and **2** have terminal electron acceptor moieties, an aldehyde in **1** and malononitrile in **2**, and compound **3** has another diphenylamino donor group. Compounds **4**, **5**, and **6** are similar to compounds **1**, **2**, and **3**, respectively, conjugated without the incorporation of phenylethynyl groups in the linkers. As the recorded absorption spectra of the structurally related compounds **1**–**6** are fundamentally different, a qualitative description of the photochemistry of these compounds in terms of molecular orbitals and the changes in electron density along the π-conjugated framework was obtained using time dependent density functional theory, TD DFT, calculations.

Although *N*-vinylcarbazoles and 3,6-functionalized carbazoles can be readily synthesized from 9*H*-carbazole, the preparation of 2,7-functionalized carbazoles is not straightforward. We report the

---

* Corresponding author. Tel.: +1 419 575 2064; fax: +1 419 372 0366; e-mail address: tkinstl@bgsu.edu (T.H. Kinstle).

0040-4020/$ – see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2010.10.050

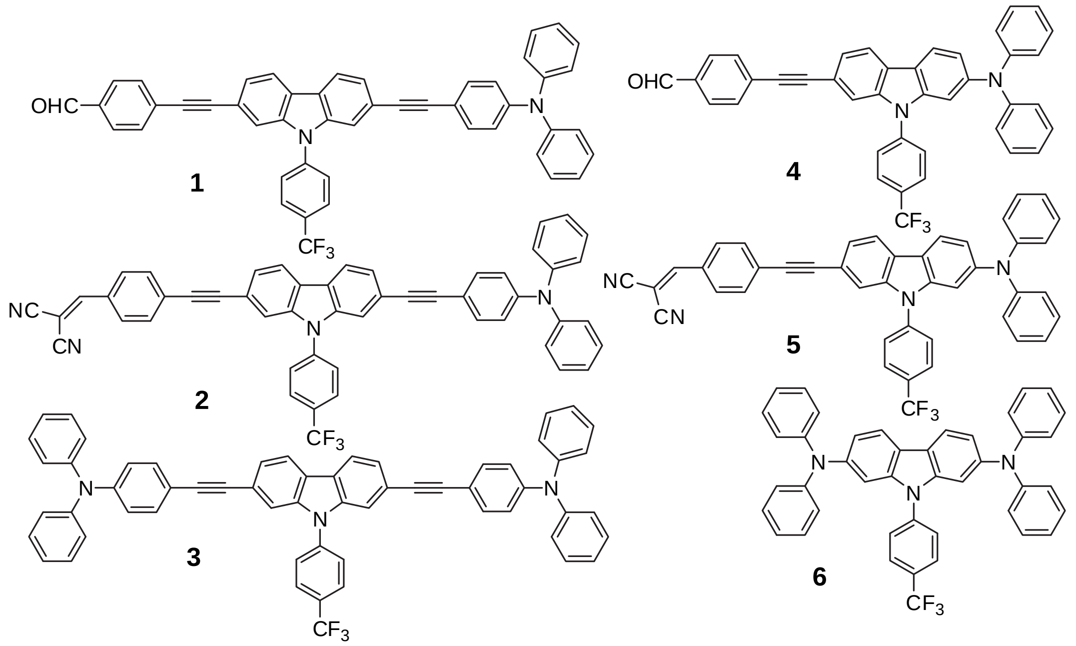


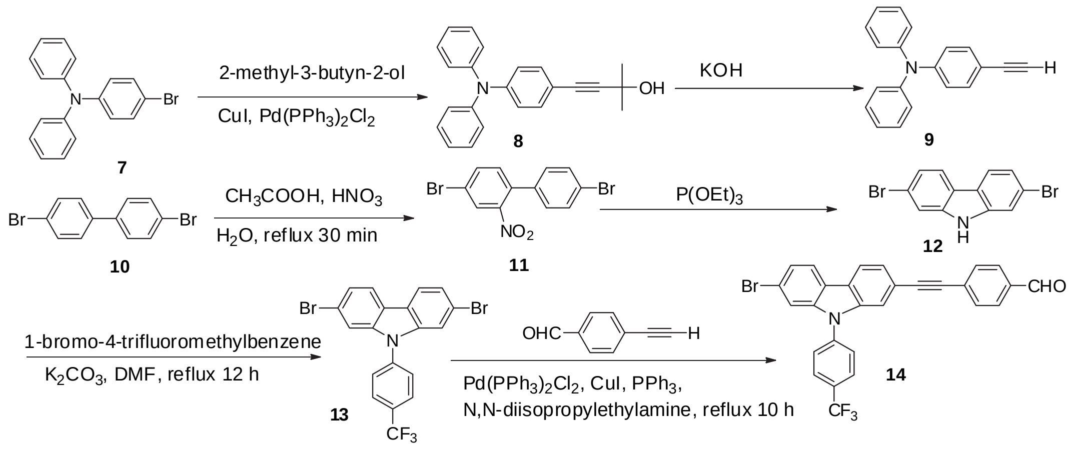
Fig. 1. Molecular structures of compounds **1**–**6**.

synthesis of 4-({7-{[4-(diphenylamino)phenyl]ethynyl}-9-[4-(trifluoromethyl)phenyl]-9*H*-carbazol-2-yl}ethynyl)benzaldehyde(**1**), [4-({7-{[4-(diphenylamino)phenyl]ethynyl}-9-[4-(trifluoromethyl)-phenyl]-9*H*-carbazol-2yl}ethynyl)benzylidene]malononitrile (**2**), 4,4′-[{9-[4-(trifluoromethyl)phenyl]-9*H*-carbazole-2,7-diyl}bis-(ethyne-2,1-diyl)]bis(*N*,*N*-diphenylaniline) (**3**), 4-({7-(diphenylamino)-9-[4-(trifluoromethyl)phenyl]-9*H*-carbazol-2-yl}ethynyl)-benzaldehyde (**4**), [4-({7-(diphenylamino)-9-[4-(trifluoromethyl) phenyl]-9*H*-carbazol-2-yl}ethynyl)benzylidene]malononitrile (**5**), and *N*,*N*,*N*′,*N*′-tetraphenyl-9-[4-(trifluoromethyl)phenyl]-9*H*-carbazole-2,7-diamine (**6**).

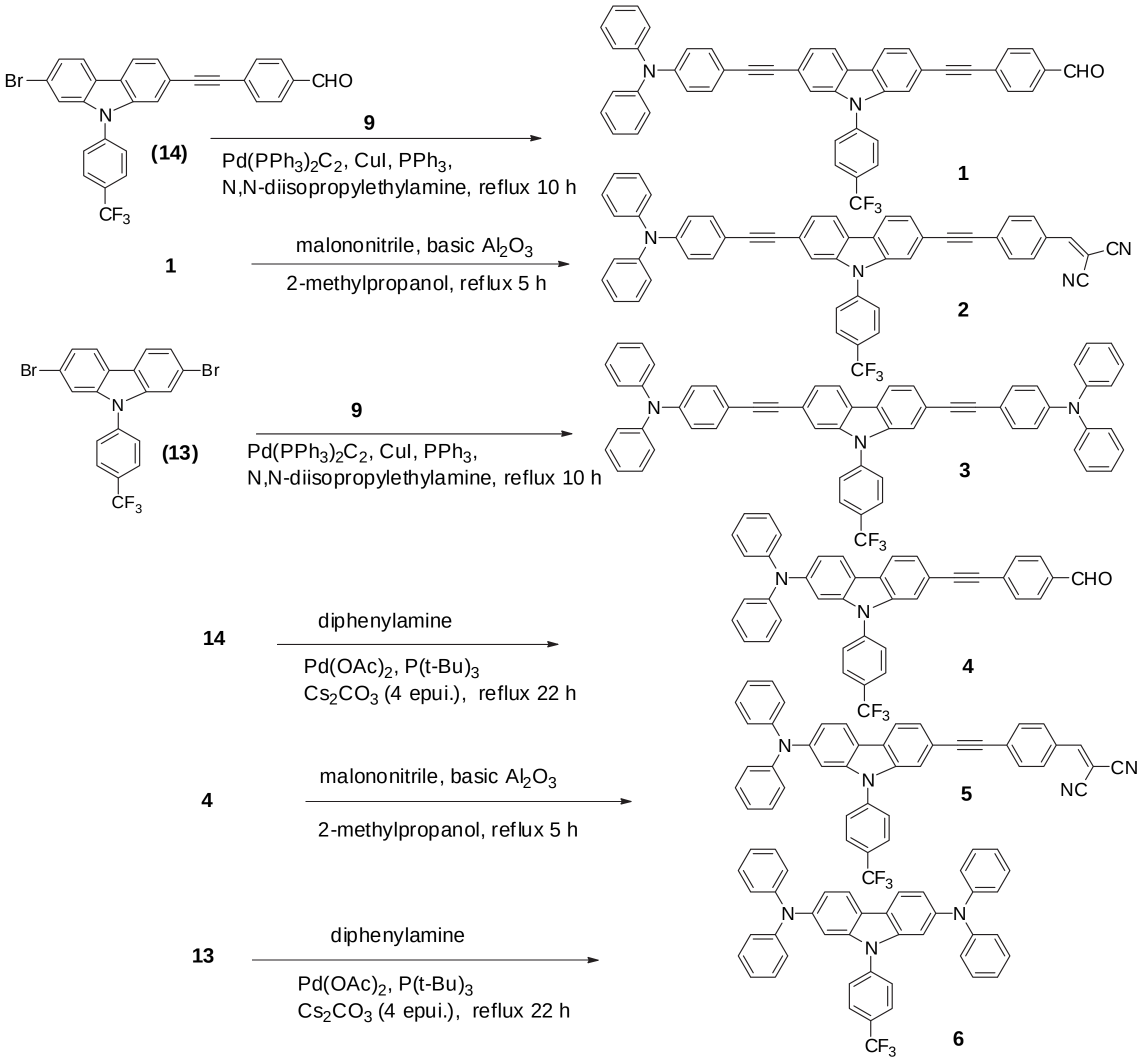
2. Results and discussion

Compound **9** (*N*-(4-ethynylphenyl)-*N*-phenylbenzenamine) was prepared from commercially available **7** (4-bromotriphenylamine) by Sonogashira coupling with 3-methylbutyn-3-ol followed by reverse addition (Scheme 1).[23] Compound **10** was converted into 2,7-dibromocarbazole (**12**) following a literature procedure.[24] N-Arylation of **12** was followed by the Sonogashira coupling with 4-ethynylbenzaldehyde to obtain **14** (Scheme 1).[25] Sonogashira coupling of **14** with **9** yielded **1**, which was further reacted with malononitrile and basic aluminum oxide in toluene to produce **2**. Sonogashira coupling of **9** with **13** produced the compound **3** (Scheme 2). Similarly, **14** was coupled with diphenylamine to produce **4**, which was further reacted with malononitrile and basic aluminum oxide in toluene to produce **5**. Diphenylamine was coupled with compound **13** under standard conditions to produce compound **6**.

The experimental and calculated absorption spectra of compounds **1**–**6** in hexanes and dichloromethane (DCM) are shown in Fig. 2. There are three major factors that are expected to affect the nature of the excited states of the reported compounds: (i) the choice of donor—held constant in this study, (ii) the presence/absence of phenylethynyl extenders, which is expected to affect—to some extent—the degree of conjugation and hence the color of these molecules, and (iii) the choice of acceptor—varied as previously outlined. The effect of incorporating phenylethynyl extenders on the UV–vis spectra of these compounds can be discerned by comparing compounds **3** and **6**, as all other variables are



Scheme 1. Synthesis of compounds **9** and **14**.



Scheme 2. Synthesis of compounds **1**–**6**.

held constant in this case. Here, incorporation of the extenders causes an increase in the ratio of intensities of the red to blue absorption bands. Although the spectra are relatively more complex, the same trend is manifested when compounds **1** and **4** on one hand, and **2** and **5** on the other hand, are compared. The effect of changing the nature of the acceptor group on the absorption spectra can be monitored by comparing compounds **1** and **4** to compounds **2** and **5**, respectively. It is not surprising that a stronger electron acceptor moiety results in an overall relatively red-shifted absorption spectrum. However, the overall changes in the absorption spectra as a function of changing the molecular and electronic structures of these compounds are more pronounced in going from compound **4** to **5**, as opposed to compound **1** to **2**. The latter is thought to be another consequence of the presence of the phenylethynyl extenders in compounds **4** and **5**, and a clear indication that the low-lying electronically excited states in these molecules not only depend on the natures of the donor and acceptor moieties, but also on the distance separating the two groups.

Because of the charge transfer character of the low-lying electronic states of compounds **1**, **2**, **4**, and **5**, the calculated stick spectra depicted in Fig. 2 reveal that the B3LYP functional and its time dependent analogue fail to correctly describe these states. Although the major goal of this report is not to accurately reproduce the measured UV–vis absorption spectra using tools of computational photochemistry, a qualitative understanding of the nature of the low-lying electronically excited states in these molecules is sought after. We thus tested the performance of another density functional, namely CAM-B3LYP, in combination with one of the most commonly used basis set for the calculation of organic compounds, see Fig. 2. The calculated TD CAM-B3LYP vertical transition energies are in very close agreement with the experimental spectra, revealing the importance of the long range correction (the Coulomb-attenuating method) to the B3LYP functional in describing the excited states of our DA type compounds.

Fig. 3 shows the highest four occupied molecular orbitals of compounds **1**–**3** calculated at the CAM-B3LYP/6-31G* level of theory. It can be directly observed that the nature of these orbitals is qualitatively similar for compounds **1**–**2** (the DA complexes), both different from compound **3** (the DD complex). Particular attention is drawn to two orbitals: (i) the HOMO where electron density is localized at the donor moiety in compounds **1**–**2** but delocalized throughout the entire π-framework in compound **3**, and (ii) the HOMO-2 orbital in compounds **1**–**2** in which electron density is localized at the carbazole moiety, this orbital relatively stabilized to become HOMO-3 in compound **3**. Moreover, the previously mentioned HOMO in compound **3** is qualitatively similar to the HOMO-1 orbitals of compounds **1** and **2**. The latter has direct implications on the photochemistry of the fundamentally different

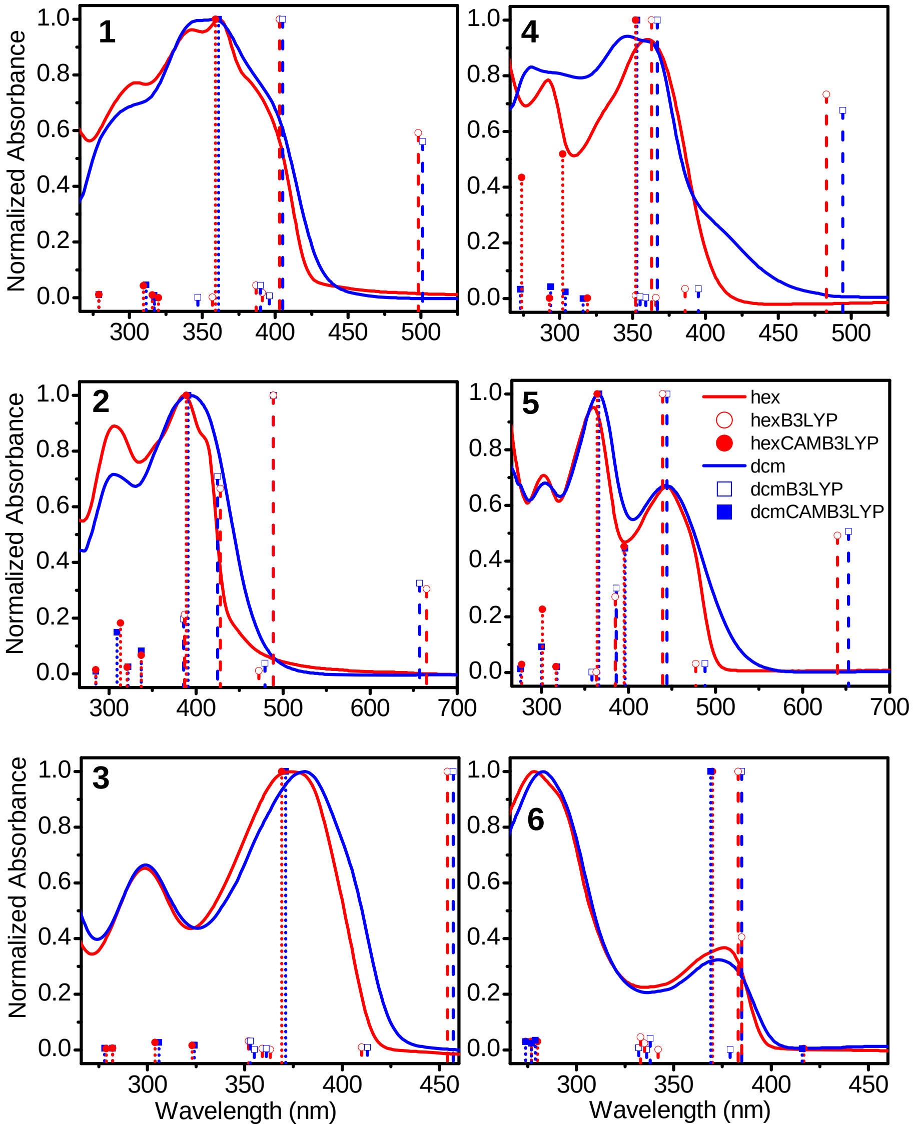


Fig. 2. Experimental and computed UV–vis absorption spectra of compounds **1**–**6**. The spectra are shown in red and blue for hexanes and DCM, respectively. The calculated vertical transition energies in hexanes and DCM are represented by circles and squares, respectively. The stick spectra were calculated using both the B3LYP (dashed bars, open symbols) and CAM-B3LYP (dotted bars, full symbols) functionals.

constructs **3** and **6**, and this will be discussed in the context of electronic transitions (vide infra). Fig. 4 shows the lowest four unoccupied molecular orbitals of compounds **1**–**3**. Here, electron density in the LUMO of compounds **1**–**2** is localized at the structurally different acceptor moieties, whereas it is delocalized over the conjugated π-framework of **3** where no acceptor was attached by design. Qualitatively similar results were obtained for compounds **4**–**6**, (see Figs. 5 and 6). One noticeable difference is that in compounds **1**–**2**, delocalization extends along the π-framework only to the linker carbazole but in compounds **4**–**5** the electron density is delocalized over the linker carbazole as well as the donor. For instance, the electron density in the HOMO of the latter mentioned compounds is delocalized over the donor as well as the carbazole moieties. These findings point out that less efficient electronic communication between the donor and acceptor is achieved when the spacers are inserted by design. In other words, electron density is 'trapped' at the donor moiety when a phenylethynyl extender is inserted between the donor and the carbazole mediator. As delocalization is expected to affect the overall color of π-conjugated systems, the effects of the presence/absence of a phenylethynyl extender on delocalization is well-documented in this work.

The assignments of the first three electronic transitions in terms of major contributing molecular orbitals of compounds **1**–**6** are summarized in Table 1. First, the lowest energy transition in compounds **1**–**2** and **4**–**5** are HOMO/LUMO donor–acceptor transitions. Second, a careful inspection of Figs. 3–6 combined with Table 1 reveals that the nature of the first two electronic transitions is similar in the DA compounds **1**, **2**, **4**, and **5**, all fundamentally different from the nature of the first two transitions in the DD compounds **3** and **6**. Third, the results of the DD compounds shed light on the fact that the trifluoromethylphenyl group does not participate in the DA-type transitions in this series of compounds unless electron density is 'confined in space' by design (for instance by inspecting the HOMO to LUMO transition in compound **6**). A careful inspection of Table 1 and Figs. 3–6 reveals that none of the molecular orbitals associated with the lowest two lying electronic transitions in compounds **1**–**2** and **4**–**5** have electron density localized at the trifluoromethylphenyl moiety. This is not the case for compounds **3** and **6** where low-energy electronic transitions

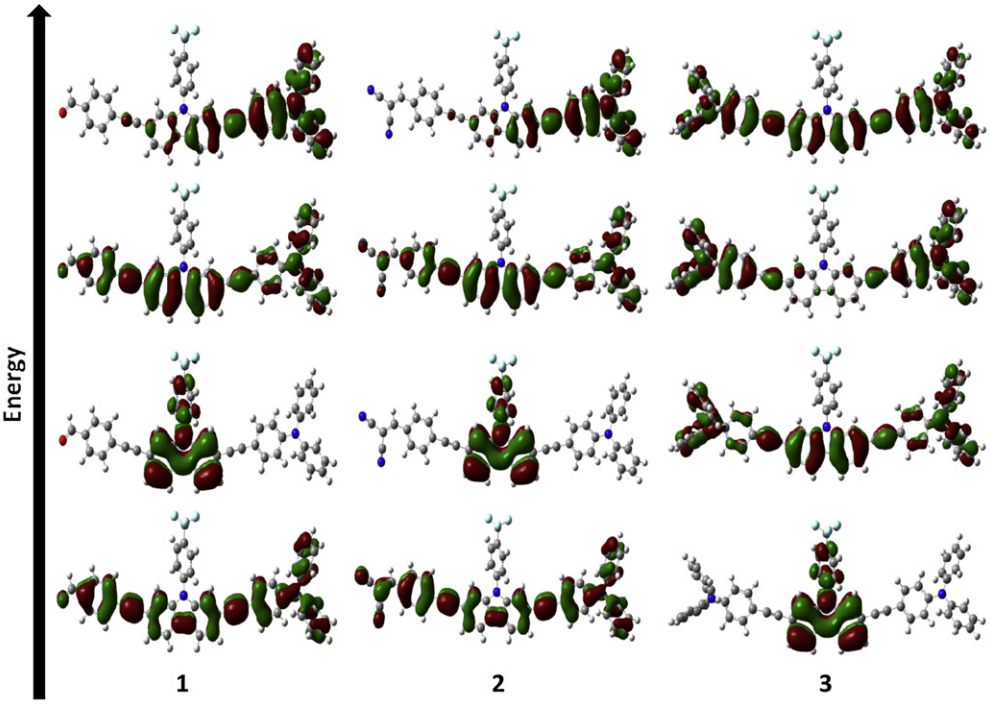


Fig. 3. The highest four occupied molecular orbitals of compounds **1**–**3** calculated at the CAM-B3LYP/6-31G* level of theory.

involve electron density shift toward the trifluoromethylphenyl group. Overall, the computational findings in this work suggest that both the nature of the acceptor moiety and the presence/absence of a spacer are expected to influence the characters of the low-lying electronic states and hence the 'colors' of these compounds. Further experimental work and computational works are needed to separate these two factors and to understand the overall photophysics/photochemistry of these systems.

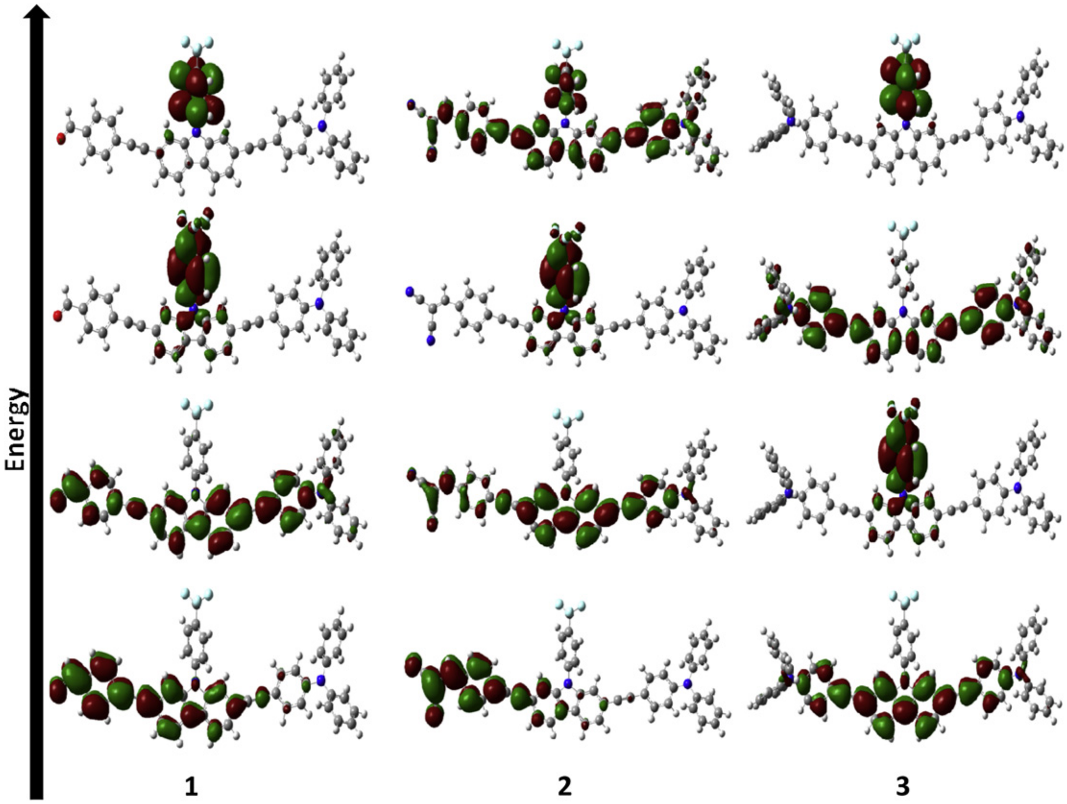


Fig. 4. The lowest four unoccupied molecular orbitals of compounds **1**–**3** calculated at the CAM-B3LYP/6-31G* level of theory.

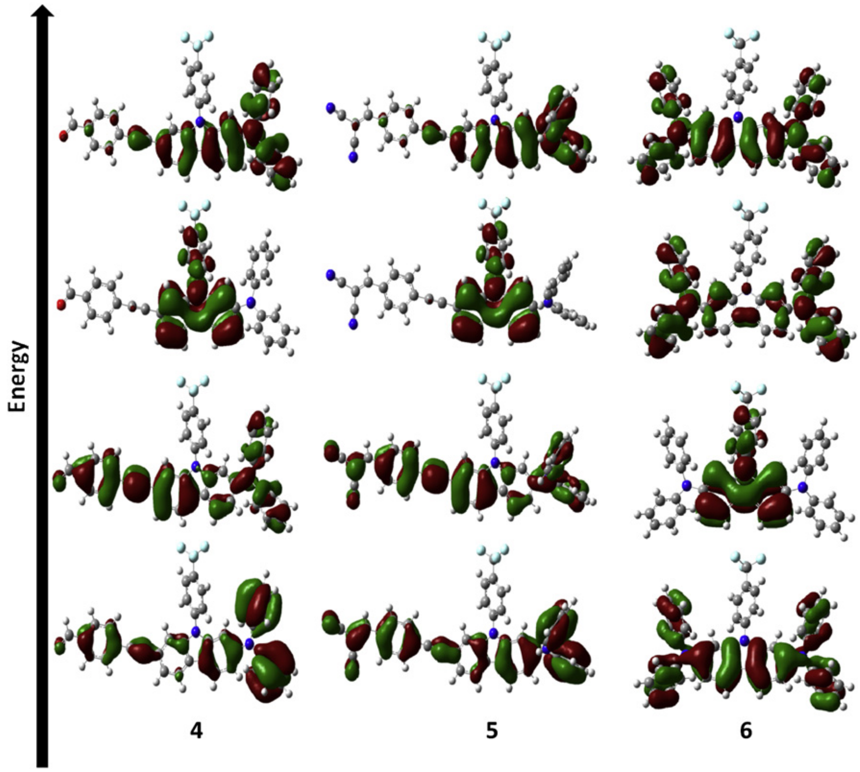


Fig. 5. The highest four occupied molecular orbitals of compounds **4**–**6** calculated at the CAM-B3LYP/6-31G* level of theory.

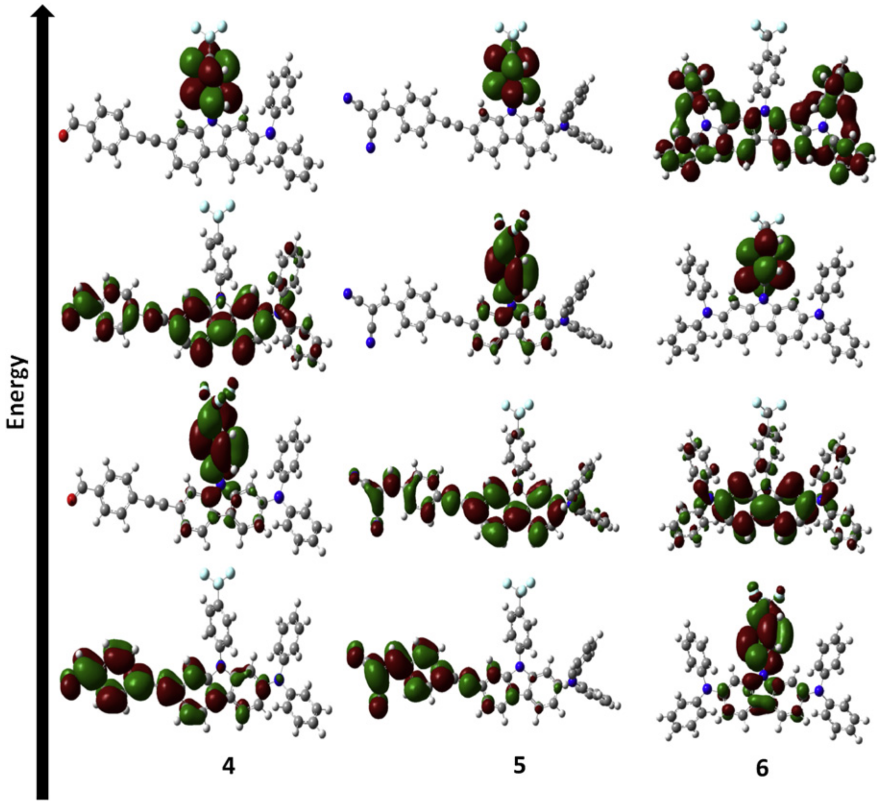


Fig. 6. The lowest four unoccupied molecular orbitals of compounds **4**–**6** calculated at the CAM-B3LYP/6-31G* level of theory.

Table 1
A description of the lowest three vertical transitions of compounds **1**–**6** in terms of major contributing molecular orbitals calculated at the CAM-B3LYP/6-31G* level of theory

	S_0/S_1	S_0/S_2	S_0/S_3
1			
Description	HOMO/LUMO	HOMO/LUMO+1	HOMO-2/LUMO
Coefficient	0.69	0.56	0.59
2			
Description	HOMO/LUMO	HOMO-1/LUMO	HOMO-2/LUMO
Coefficient	0.7	0.65	0.7
3			
Description	HOMO/LUMO	HOMO-1/LUMO	HOMO/LUMO+1
Coefficient	0.67	0.68	0.7
4			
Description	HOMO/LUMO	HOMO-1/LUMO	HOMO/LUMO+1
Coefficient	0.68	0.68	0.7
5			
Description	HOMO/LUMO	HOMO-1/LUMO	HOMO-2/LUMO
Coefficient	0.69	0.7	0.64
6			
Description	HOMO/LUMO	HOMO/LUMO+1	HOMO/LUMO+2
Coefficient	0.7	0.67	0.7

3. Conclusions

The synthesis of a novel series of organic donor–acceptor compounds with a diphenylamine donor, 2,7-functionalized carbazole-based linkers, and either (i) an aldehyde, (ii) malononitrile, or (iii) diphenylamino acceptors—all with and without phenylethynyl extenders—is reported. An insight into the nature of the first three electronic transitions in these compounds is obtained from DFT and TD DFT calculations. Results suggest that in this series, less efficient electronic communication between the donor and acceptor is achieved when the phenylethynyl groups are inserted. The latter has direct implications on the overall color of the compound in the reported series. It can also be argued that electron density is trapped at the extender itself: the extender, rather than increasing conjugation/delocalization, inhibits it by holding electron density locally. Moreover, which major contributing molecular orbitals are involved in low-lying electronic transitions is found to depend on both (i) the nature and choice of the acceptor group, and (ii) the presence/absence of a phenylethynyl group in the linker.

4. Experimental and computational methods

4.1. Synthesis

General: All solvents and reagents were of reagent grade quality and used without further purification unless stated otherwise. All reactions and manipulations were carried out under argon gas with the use of standard inert atmosphere techniques. Starting materials diphenylamine, **7** and **10** were purchased. The precursor of targeted compound **9** was prepared by adapting literature procedure.[23] The synthetic procedures of compounds **12** and **13** are described elsewhere.[24,25] New synthetic procedures for synthesis of **1**–**6** and **14** are described here. ^{1}H and ^{13}C NMR spectra were recorded at 500 MHz using tetramethylsilane as the internal standard. The general synthetic methodologies are outlined in Schemes 1 and 2.

*4.1.1. Synthesis of 4-(2-(7-bromo-9-(4-(trifluoromethyl)phenyl)-9H-carbazol-2-yl)ethynyl)benzaldehyde (**14**).* To a solution of compound **13** (1 g, 2.13 mmol) in dry diisopropylethylamine (12 mL) was added 4-ethynylbenzaldehyde (0.24 g). After the solution was degassed with argon for 30 min while stirring, $Pd(PPh_3)_2Cl_2$ (15 mg), triphenylphosphine (10 mg), CuI (11 mg), and compound **5** were added. The reaction mixture was then refluxed under argon for 10 h. After the reaction was completed, the crude mixture was filtered at room temperature the precipitate was rinsed with diethyl ether and the combined filtrates were evaporated. The residue was purified by flash column chromatography (silica gel, 20% ethyl acetate in petroleum ether) to give compound **8** (51%) as a yellowish solid. Mp: 211 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47 (dd, 1H), 7.54 (dd, 1H), 7.58 (d, 2H), 7.70 (d, 2H), 7.74 (d, 2H), 7.87 (s, 1H), 7.90 (s, 1H), 7.96 (d, 2H), 8.01 (d, 1H), 8.12 (d, 1H), and 10.05 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 89.0, 94.0, 112.9, 113.2, 120.4, 120.6, 120.7, 121.9, 122.2, 123.6, 124.3, 124.8, 127.3, 127.5, 127.6, 129.6, 132.1, 135.5, 140.3, 141.9, and 191.3. HRMS (EI) calculated for $C_{28}H_{15}ONBrF_3$ 517.0289, measured 517.0287.

*4.1.2. Synthesis of 4-({7-{[4-(diphenylamino)phenyl]ethynyl}-9-[4-(trifluoromethyl)phenyl]-9H-carbazol-2-yl}ethynyl)benzaldehyde (**1**).* To a solution of compound **14** (100 mg, 0.19 mmol) in dry diisopropylethylamine (6 ml) was added compound **9** (52 mg, 0.19 mmol). After the solution was degassed with argon for 30 min while stirring, $Pd(PPh_3)_2Cl_2$ (5 mg), triphenylphosphine (5 mg), and CuI (5 mg) were added. The reaction mixture was then refluxed under argon for 10 h. After the reaction was completed, the crude mixture was filtered at room temperature, the precipitate was rinsed with diethyl ether, and the combined filtrates were evaporated. The residue was purified by flash column chromatography (silica gel, 20% ethyl acetate in petroleum ether) to give compound **1** (92 mg, 67% yield) as a shining yellow solid. Mp: 197 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.03 (d, 2H), 7.09 (t, 2H), 7.14 (dd, 4H), 7.3 (dd, 4H), 7.4 (d, 2H), 7.52 (dd, 1H), 7.55 (dd, 1H), 7.58 (s, 1H), 7.62 (s, 1H), 7.71 (d, 2H), 7.78 (d, 2H), 7.89 (d, 2H), 7.96 (d, 2H), 8.11 (d, 1H), 8.14 (d, 1H), and 10.05 (s, 1H). ^{13}C NMR (500 MHz, $CDCl_3$): 88.92, 89.4, 94.2, 105.3, 113.2, 119.9, 120.6, 120.7, 122.0, 122.9, 123.6, 124.1, 124.3, 124.8, 126.9, 127.3, 129.3, 129.6, 132.0, 132.1, 140.2, 147.9, and 191.4. HRMS (MALDI-TOF) MS ES$^+$=707.231 measured, and 707.231 for theoretical spectrum having molecular formula $C_{48}H_{30}N_2OF_3$.

*4.1.3. Synthesis of [4-({7-{[4-(diphenylamino)phenyl]ethynyl}-9-[4-(trifluoromethyl)phenyl]-9H-carbazol-2-yl}ethynyl)benzylidene]malononitrile (**2**).* In a dry two necked round bottomed flask was added compound **1** (100 mg, 0.14 mmol), malononitrile (9.4 mg, 1.1 mmol), basic aluminum oxide (10 mmol), and dry toluene (10 ml). The mixture was refluxed under argon for 5 h. The mixture was filtered hot, and the residue was washed several times with hot ethyl acetate. The filtrate was then dried, and the solid obtained was purified by chromatography (silica gel, 20% ethyl acetate in petroleum ether) to obtain pure compound **2** (90 mg, 86% yield) as a reddish brown solid. Mass spectrum (MALDI-TOF) m/z M$^+$=754. Mp: 203 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.03 (d, 2H), 7.09 (t, 2H), 7.14 (d, 4H), 7.3 (t, 4H), 7.4 (d, 2H), 7.52 (dd, 1H), 7.55 (dd, 1H), 7.58 (s, 1H), 7.62 (s, 1H), 7.68 (d, 2H), 7.76 (s, 1H), 7.78 (d, 2H), 7.92 (d, 2H), 7.97 (d, 2H), 8.12(d, 1H), and 8.14 (d, 1H). ^{13}C NMR (500 MHz, $CDCl_3$): 82.7, 89.3, 90.6, 96.2, 112.6, 112.7, 113.2, 119.8, 120.8, 122.2, 122.8, 123.7, 124.2, 124.7, 125.1, 127.3, 127.4, 127.5, 129.4, 130.0, 130.2, 130.7, 132.4, 132.5, 140.6, 147.1, and 158.5.

*4.1.4. Synthesis of 4,4′-[{9-[4-(trifluoromethyl)phenyl]-9H-carbazole-2,7-diyl}bis(ethyne-2,1-diyl)]bis(N,N-diphenylaniline) (**3**).* To a solution of **13** (61 mg, 0.13 mmol) in dry diisopropylethylamine (6 ml) was added **9** (100 mg, 0.26 mmol). After the solution was degassed with argon for 30 min while stirring, $Pd(PPh_3)_2Cl_2$ (1 mg), triphenylphosphine (1 mg), and CuI (1 mg) were added. The reaction mixture was then refluxed under argon for 6 h. After the reaction was completed, the crude mixture was filtered at room temperature, the precipitate was rinsed with diethyl ether, and the combined filtrates were evaporated. The residue was purified by flash column chromatography (silica gel, 10% ethyl acetate in petroleum ether) to give pure **3** (78% yield) as a yellow solid. Mp: 88 °C. Mass spectrum (MALDI-TOF) m/z M^+=845. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.03 (d, 4H), 7.09 (t, 4H), 7.14 (d, 8H), 7.3 (t, 8H), 7.4 (d, 4H), 7.5 (dd, 2H), 7.57 (dd, 2H), 7.77 (d, 2H), 7.96 (d, 2H), and 8.1 (d, 2H). ^{13}C NMR (500 MHz, $CDCl_3$): 106.3, 117.8, 119.4, 119.8, 120.6, 121.0, 121.1, 122.5, 122.6, 123.6, 123.8, 124.0, 126.4, 127.0, 127.1, 127.2, 127.3, 127.4, 141.7, 143.1, 146.0, and 148.1.

*4.1.5. Synthesis of 4-({7-(diphenylamino)-9-[4-(trifluoromethyl)-phenyl]-9H-carbazol-2-yl}ethynyl)benzaldehyde (**4**).* Compound **14** (200 mg, 0.38 mmol) and diphenylamine (60 mg, 0.38 mmol) were mixed with dry toluene (80 ml) in a two necked round bottomed flash containing a stir bar. The $Pd(OAc)_2$ (3 mol %), $P(t\text{-}Bu)_3$ (7 mol %), and Cs_2CO_3 (495 mg, 1.52 mmol) were also added and the mixture was stirred under argon at 110 °C for about 10 h. The reaction mixture was then cooled to room temperature and toluene was removed completely under vacuum. The solid mixture was dissolved in tetrahydrofuran, and unreacted Cs_2CO_3 was removed under gravity filtration. The organic residue was then purified by column chromatography (silica gel, 10% ethyl acetate in petroleum ether) to give the yellow compound **4** (180 mg, 77% yield). Mp: 142 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.05 (t, 2H), 7.1 (dd, 1H), 7.13(d, 4H), 7.14 (d, 1H), 7.27 (d, 4H), 7.51 (dd, 1H), 7.57 (s, 1H), 7.64 (d, 2H), 7.7 (d, 2H), 7.7.83 (d, 2H), 7.89 (d, 2H), 8.0 (d, 1H), 8.4 (d, 1H), and 10.03 (s, 1H). ^{13}C NMR (500 MHz, $CDCl_3$): 82.5, 88.7, 90.6, 96.9, 105.2, 112.9, 118.4, 118.7, 118.9, 119.9, 121.5, 123.0, 124.2, 124.8, 126.9, 127.3, 129.1, 129.3, 130.0, 130.2, 130.7, 132.3, 140.3, 142.3, 147.8, and 158.5. HRMS (EI) calculated for $C_{40}H_{25}ON_2F_3$ 606.1919, measured 606.1910.

*4.1.6. Synthesis of [4-({7-(diphenylamino)-9-[4-(trifluoromethyl)phenyl]-9H-carbazol-2-yl}ethynyl)benzylidene]malononitrile (**5**).* The synthetic procedure is exactly same as for the synthesis of **2**, but using **4** as the starting material. The product was obtained after purification by column chromatography (silica gel, 20% ethyl acetate in petroleum ether) as an orange solid **5** (82% yield). Mp: 212 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.05 (t, 2H), 7.1 (dd, 1H), 7.14 (d, 4H), 7.15 (d, 1H), 7.27 (d, 4H), 7.51 (dd, 1H), 7.57 (s, 1H), 7.66 (d, 2H), 7.68 (d, 2H), 7.75 (s, 1H), 7.84 (d, 2H), 7.92 (d, 2H), 8.0 (d, 1H), and 8.05 (d, 1H). ^{13}C NMR (500 MHz, $CDCl_3$): 82.5, 88.7, 90.6, 96.9, 105.2, 112.9, 118.4, 118.7, 118.9, 119.9, 121.5, 123.0, 124.2, 124.8, 126.9, 127.3, 129.1, 129.3, 130.0, 130.2, 130.7, 132.3, 140.3, 142.3, 147.8, and 158.5. HRMS (TOF MS ES^+) calculated for $C_{43}H_{26}N_4F_3$ 655.21, measured 655.20.

*4.1.7. Synthesis of N,N,N′,N′-tetraphenyl-9-[4-(trifluoromethyl)phenyl]-9H-carbazole-2,7-diamine (**6**).* Compound **13** (200 mg, 0.38 mmol) and diphenylamine (120 mg, 0.77 mmol) were mixed with dry toluene (80 ml) in a two necked round bottomed flash containing a stir bar. The $Pd(OAc)_2$ (3 mol %), $P(t\text{-}Bu)_3$ (7 mol %), and Cs_2CO_3 (495 mg, 1.52 mmol) were also added and stirred under argon at 110 °C for about 18 h. The reaction mixture was then cooled to room temperature and toluene was removed completely under vacuum. The solid mixture was dissolved in tetrahydrofuran and unreacted Cs_2CO_3 was removed under gravity filtration. The organic residue was then purified by column chromatography (silica gel, 10% ethyl acetate in petroleum ether) to give the yellowish white product (180 mg, 77% yield). ^{1}HMR (500 MHz, $CDCl_3$): δ7.01 (t, 4H), 7.07 (dd, 2H), 7.10 (dd, 8H), 7.15 (d, 2H), 7.25 (t, 8H), 7.7.52 (d, 2H), 7.69 (d, 2H), and 7.93 (d, 2H). ^{13}C NMR (500 MHz, $CDCl_3$): 106.3, 117.8, 119.4, 119.8, 120.6, 121.0, 121.1, 122.5, 122.6, 123.6, 123.8, 124.0, 126.4, 127.0, 127.1, 127.2, 127.3, 127.4, 141.7, 143.1, 146.0, and 148.1. ^{13}C NMR (500 MHz, $CDCl_3$): 106.3, 117.9, 119.4, 119.8, 120.6, 121.1, 122.5, 123.6, 123.8, 126.4, 127.0, 127.3, 129.2, 129.4, 141.7, 143.1, 146.1, and 148.1.MS (EI^+) for $C_{43}H_{30}N_3F_3$ calculated 645.2391, measured 645.2391.

4.2. Computational methodology

Unconstrained geometry optimization was used to locate the global minima of compounds (**1**–**6**) on the ground state potential energy surface. Geometry optimization was first performed using the B3LYP density functional in combination with the commonly used 6-31G* basis set.[26] These calculations were performed in the vacuum, hexanes, and DCM—the solvent environments treated using the polarizable continuum solvation (PCM) model. Using the fully optimized B3LYP/6-31G* minima, vertical transition energies were computed at the TD B3LYP/6-31G* level of theory, Table S1 of the ‘Supplementary data’ section of this work. The B3LYP functional is the standard methodology for simulating various processes in organic chemistry because it offers a good compromise between computational cost and accuracy in the prediction of a variety of molecular properties.[27] However, as the low-lying electronic transitions in these compounds involve a large change in electron density or intramolecular charge transfer (vide infra), the approximation in the level of theory used in this work has little to do with the choice of basis set and mainly comes from the density functional.[28] This is especially true for the first electronic (HOMO/LUMO) transition in the reported D–A complexes where electron density shifts across these molecules from the donor moiety (D) to the acceptor moiety (A) through different lengths of π-conjugated mediators. However, these calculations provide a framework for a qualitative comparative description of the electronic transitions in compounds (**1**–**6**) in terms of molecular orbitals and the changes in electron density accompanying electronic transitions. These results are discussed in the ‘Results and discussion’ section of this work.

There is a growing need to obtain more quantitative agreement between the calculated and experimental spectra of such DA type compounds. This is why we also tested a more recently developed long range corrected version of the B3LYP hybrid functional, namely the CAM-B3LYP functional.[29] The CAM-B3LYP/6-31G* calculations yield a more quantitative agreement with the experimental spectra, Table S1 and S2 of the ‘Supplementary data’ section of this work. All calculations reported in this work were performed using the methodologies developed in the Gaussian 2009 package.[30]

Acknowledgements

This present work has been partially supported by Grant NSF-EXP 40000/10380080. We thank the donors of these funds. An allocation of computing time from the Ohio Supercomputer Center is acknowledged.

Supplementary data

^{1}H and ^{13}C NMR spectra of compound **1**–**6** and **14**, and the calculated TD DFT vertical transition energies of compounds **1**–**6**. Supplementary data associated with this article can be found in online version at doi:10.1016/j.tet.2010.10.050.

References and notes

1. Sun, X.; Liu, Y.; Xu, X.; Yang, C.; Yu, G.; Chen, S.; Zhao, Z.; Qiu, W.; Li, Y.; Zhu, D. *J. Phys. Chem. B* **2005**, *109*, 10786 and references therein.
2. Schon, J. H.; Kloc, C.; Bucher, E.; Batlogg, B. *Nature* **2000**, *403*, 408.
3. Mitschke, U.; Bauerle, P. *J. Mater. Chem.* **2000**, *10*, 1471.
4. Yeh, H.-C.; Chan, L.-H.; Wu, W.-C.; Chen, C.-T. *J. Mater. Chem.* **2004**, *14*, 1293.
5. Hughes, A. G.; Bryce, M. R. *J. Mater. Chem.* **2005**, *15*, 94.
6. Hara, K.; Sato, T.; Katoh, R.; Furube, A.; Ohga, Y.; Shinpo, A.; Suga, S.; Sayama, K.; Sugihara, H.; Arakawa, H. *J. Phys. Chem. B* **2003**, *107*, 597.

7. Hagberg, D. P.; Edvinsson, T.; Marinado, T.; Boschloo, T.; Hagfeld, A.; Sun, L. *Chem. Commun.* **2006**, 2245.
8. Loiseau, F.; Campagna, S.; Hameurlaine, A.; Dehaen, W. *J. Am. Chem. Soc.* **2005**, *127*, 11352.
9. Stampor, W.; Mroz, W. *Chem. Phys.* **2007**, *331*, 261.
10. Joule, J. A. *Adv. Heterocycl. Chem.* **1984**, *35*, 83.
11. Zhu, Z.; Moore, J. S. *J. Org. Chem.* **2000**, *65*, 116.
12. Li, Z. H.; Wong, M. S. *Org. Lett.* **2006**, *8*, 1499.
13. Huang, S.; Hsu, Y.; Yen, Y.; Chou, H.; Lin, J. T.; Chang, C.; Hsu, C.; Tsai, C.; Yin, D. *J. Phys. Chem. C* **2008**, *112*, 19739.
14. Ko, C.-W.; Tao, Y.-T.; Lin, J. T.; Thomas, K. R. J. *Chem. Mater.* **2002**, *14*, 357.
15. Siove, A.; Ades, D. *Polymer* **2004**, *45*, 4045.
16. Kim, J. K.; Hong, S. I.; Cho, H. N.; Kim, D. Y.; Kim, C. Y. *Polym. Bull.* **1997**, *38*, 169.
17. Blouin, N.; Michaud, A.; Leclerc, M. *Adv. Mater.* **2007**, *19*, 2295.
18. Morin, J.-F.; Leclerc, M. *Macromolecules* **2001**, *34*, 4680.
19. Morin, J.-F.; Drolet, N.; Tao, Y.; Leclerc, M. *Chem. Mater.* **2004**, *16*, 4626.
20. Sonntag, M.; Strohriegl, P. *Chem. Mater.* **2004**, *16*, 4736.
21. Promarak, V.; Ruchirawat, S. *Tetrahedron* **2007**, *63*, 1602.
22. Shao, H.; Chen, X.; Wang, Z.; Lu, P. *J. Lumin.* **2007**, *127*, 349.
23. Panthi, K.; Adhikari, R. M.; Kinstle, T. H. *J. Phys. Chem. A* **2010**, *114*, 4542.
24. Dierschke, F.; Grimsdale, A. C.; Mullen, K. *Synthesis* **2003**, 2470.
25. Panthi, K.; Adhikari, R. M.; Kinstle, T. H. *J. Phys. Chem. A* **2010**, *114*, 4550.
26. Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257.
27. Riley, K. E.; Op't Holt, B. T.; Merz, K. M., Jr. *J. Chem. Theory Comput.* **2007**, *3*, 407.
28. Jensen, J. *Introduction to Computational Chemistry*, 2nd ed.; Wiley: Chichester, England, 2006.
29. Yanai, T.; Tew, D. P.; Handy, N. C. *Chem. Phys. Lett.* **2004**, *393*, 51.
30. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. Gaussian 03, Revision C.02; Gaussian: Wallingford, CT, 2009.