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N, N-DIMETHYL AMINE LINKED TO TRIPHENYLAMINE (TPA): A PROMISING CO-DONOR MOIETY IN ORGANIC DYES AND THEIR PUSH-PULL BEHAVIOR

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Pág. 57-65

Abstract

The push-pull behavior of novel codonor-donor dyes bearing a *N,N*-dimethyl amine linked covalently to a triphenylamine group through a vinyl bridge was studied by experimental (electrochemical and spectroscopic) analysis. These dyes were obtained by conventional reactions using a convergent synthesis method. An intra-molecular charge transfer process was observed in the electronic structure of these compounds.

Keywords: dyes, triphenylamine, push-pull, donor, acceptor.

1 Introduction

The intra-molecular electronic communication between electron donor and acceptor units is an important topic in chemistry since it is a key issue in a wide variety of different areas such as electrically conducting materials, non-linear optics (NLO), molecular rectification, dyes, photovoltaics (PV) [1], etc.

The triphenylamine (TPA) derivatives are most widely used as electron donors for metal-free organic dyes because their excellent molecular configuration and non-planar aggregation resistance. Aggregation can lead to auto-off, instability of the dye, and a reduction in the efficient electronic injection [2]. Several molecules (**1**-**6**) have been synthesized containing the fragment TPA as an electron donor (figure 1). Different approaches have been explored to connect this electro-active unit with a diverse number of electron acceptor species [3-7]. The dyes described above have showed efficiencies of solar energy to electrical energy conversion between 2.3% to 8.01% [8].

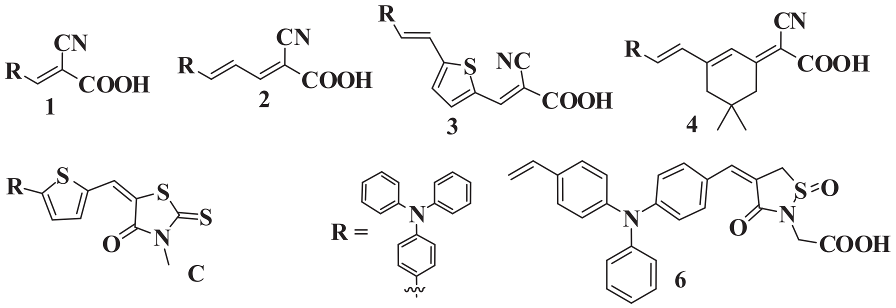


Figure 1. *Chemical Structure of several organic dyes based in TPA (***1**-**6***).*

Fullerene C_{60} and their derivatives, however, exhibit a number of diverse electronic and photophysical properties, which have been investigated for application in new molecular electronic devices. Fullerenes are good acceptors in the excited state, various electron-donor units attached to this molecule, are expected to photoinduced intramolecular charge transfer [9].

2 Methodology and experimental procedure

Commercially available starting materials, reagents and solvents were used as supplied. Solvents used in photochemical measurements were of spectroscopic grade. TLC analysis were performed on Merck TLC plates silica gel 60 F254, melting points were determined in a Buchi Melting Point Apparatus and were uncorrected. The ^{1}H and ^{13}C NMR spectra were run on a Bruker AVANCE 400 spectrometer operating at 400 MHz and 100 MHz respectively, using chloroform-*d* as solvent and tetramethylsilane as internal standard.

The mass spectra were scanned on a Shimadzu MS-QP 2010 spectrometer operating at 70 eV. UV-vis spectra were recorded in a Shimadzu 1700 spectrometer. Electrochemical measurements were performed on an auto-lab PGStat 30 equipment using a three-electrode configuration system. The measurements were carried out using a CH_2Cl_2 solution of 0.1 M in tetra-butyl ammonium perchlorate as supporting electrolyte. A glassy carbon electrode (3 mm diameter) was used as the working electrode, and a platinum wire and an $Ag/AgNO_3$ electrode were employed as the counter and the reference electrodes, respectively.

The surface of the working electrode was polished with commercial alumina prior to use. Solutions were deaerated by bubbling argon for a few minutes prior to each voltammetry measurement. Unless otherwise specified the scan rate was 100 mVs^{-1}, the Fc/Fc$^+$ system was used as internal standard.

2.1 Preparation of (*E*)-4-((4-(4-(dimethyl amine)styryl)phenyl)(phenyl)amino) benzaldehyd (9)

In a 25 mL two-necked flask, 248 mg (0.82 mmol) of 4,4´-di-formyl tri-phenyl amine **8** and 308 mg of *t*-BuOK were weighed and then, were dissolved in dry THF (5.0 mL), the reaction mixture was heated at 81 °C under argon atmosphere for 10 minutes. After that, 149 mg (0.55 mmol) of phosphonate of *N,N*-dimethyl amine benzyl 7 were dissolved in dry THF and were added to the reaction mixture via syringe dropwise over a period of 30 min. The reaction was allowed to warm for 8 hours, After removal of the solvents under reduced pressure, the residue was purified by column chromatography (silica gel, dichloromethane) to afford **9** as a yellow oil, 57% yield.

^{1}H -NMR (400 MHz, $CDCl_3$) δ: 9.85 (s, 1H), 7.72 (d, J_o=8.0 Hz, 2H), 7.46 (m, 4H), 7.38 (d, *J*=8.0 Hz, 2H), 7.22 (m, 3H), 7.15 (d, *J*=8.0 Hz, 2H), 7.09 (d, *J*=8.0 Hz, 2H), 7.05 (d, *J*=16.0 Hz, 1H), 6.92 (d, *J*=16.0 Hz, 1H), 6.76 (d, *J*=8.0 Hz, 2H), 3.03 (s, 6H) ppm; ^{13}C -NMR (100 MHz, $CDCl_3$) δ: 190.5, 153.3, 150.2, 146.1, 144.6, 135.2, 131.4, 129.8, 129.1, 128.8, 127.6, 127.2, 126.3, 125.7, 125.1, 123.4, 119.6, 112.5, 77.4, 77.1, 76.8, 40.5, 29.8 ppm; FT-IR (KBr). υ(cm^{-1}) = 3418, 2922, 2852, 1726, 1690, 1602, 1586, 1522, 1503, 1488, 1356, 1325, 1283, 1219, 1189, 1160, 1056,. MS-EI: *m*/*z* 418 [M]$^+$.

2.2 Preparation of Dye Co-D-Ac

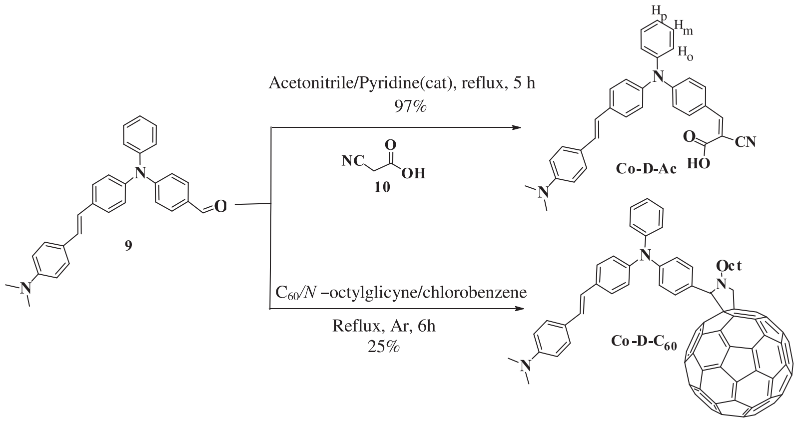
In a 10 mL round bottom flask, 53 mg (0.127 mmol) of **9** with 21.6 mg (0.253 mmol) of cyano-acetic acid **10,** were dissolved in 5.0 mL of acetonitrile and allowed to reflux by addition drop to drop 1.0 mL of pyridine, the reaction mixture was heated for 5h. When the reaction finished, the reactants were filtered and the precipitate was washed with hexane and ethyl ether to obtain an orange solid, 98% of yield. ^{1}H -NMR (400 MHz, DMSO-d_6) δ: 7.85 (s, 1H), 7.78 (d, *J* = 8.0 Hz, 2H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.40 (m, 4H), 7.19-7.13 (m, 3H), 7.09-7.05 (m, 3H), 6.97-6.93 (m, 3H), 6.72 (d, *J* = 8.0 Hz, 2H), 2.93 (s, 6H) ppm; ^{13}C -NMR (100 MHz, DMSO-d_6) δ: 130.9, 129.8, 127.4, 127.1, 125.4, 125.3, 112.3, 54.9, 40.1, 39.9, 39.7, 39.5, 39.3, 39.0, 38.8, 24.7 ppm; FTIR (KBr). υ(cm^{-1}) = 3449, 2922, 2851, 2212, 1602, 1584, 1524, 1504, 1488, 1415, 1387, 1359, 1326, 1286, 1220, 1178, 1059, 1021,. MS-EI: *m*/*z* 485 [M]$^+$.

2.3 Preparation of Dye Co-D-C_{60}

In a 50 mL two-necked flask, 138 mg (0.19 mmol) of fullerene C_{60} in 10.0 mL of chloro-benzene was dissolved by sonication. Then 54 mg (0.29 mmol) of N-octylglycine and 40 mg (0.10 mmol) of 9 were added. The reaction mixture was heated to reflux with a Dean-Stark tramp for 8 h. After the solvent was evaporated under reduced pressure, the reaction crude was purified by column chromatography (silica gel, hexane:CS_2, 2:1), to afford a brown solid, 25% yield. ^{1}H -NMR (400 MHz, $CDCl_3$) δ: 7.73-7.41(m, 2H), 7.29 (d, *J* = 12.0 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.16- 7.09 (m, 3H), 7.04 (d, *J* = 8.0 Hz, 2H), 6.96-6.93 (m, 2H), 6.91-6.88 (m, 2H), 6.85 (d, *J* = 16.0 Hz, 1H), 6.76 (d, *J* = 16.0 Hz, 1H), 6.63 (d, *J* = 12.0 Hz, 2H), 5.01 (d, *J* = 8.0 Hz, 1H), 4.95 (s, 1H), 4.04 (d, *J* = 8.0 Hz, 1H), 2.89 (s, 6H), 1.49-1.18 (m, 14H), 0.84 (t, *J* = 16.0 Hz, 3H) ppm; ^{13}C -NMR (100 MHz, CDCl$_3$) δ: 154.3, 154.0, 153.7, 147.8, 147.5, 147.4, 147.0, 146.6, 146.5, 146.3, 146.2, 146.1, 146.0, 145.8, 145.6, 145.5, 145.4, 145.3, 145.2, 144.8, 144.4, 143.2, 143.0, 142.7, 142.6, 142.4, 142.3, 142.2, 142.1, 141.8, 141.7, 141.6, 140.2, 140.1, 139.2, 139.2, 136.8, 136.7, 136.5, 136.4, 135.9, 135.8, 132.9, 131.7, 129.3, 128.3, 127.6, 127.4, 126.9, 126.1, 124.2, 123.9, 122.9, 112.6, 82.1, 77.4, 77.1, 76.7, 68.9, 66.9, 40.6, 32.0, 29.8, 29.4, 28.5, 27.7, 22.8, 14.3 ppm; FTIR (KBr). υ(cm^{-1}) = 3423, 2920, 2850, 2791, 1603, 1519, 1503, 1459, 1353, 1314, 1275, 1216, 1167, 1114, 1066, 1021, 952, 819, 798, 752, 694, 616, 597, 576, 545, 524, 453, 423, 402.

3. Results and discussion

We first explored the synthesis of compounds **Co-D-Ac** and **Co-D-C$_{60}$** by a routine procedure in a multistep methodology (Scheme 1).



Scheme 1. *Synthesis of compounds* **Co-D-Ac** *and* **Co-D-C$_{60}$**.

Initially, we synthesized the codonor-donor unit by a Horner-Wadsworth-Emmons reaction, using phosphonate of *N,N*-dimethylaminebenzyl **7** and *t*-BuOK as base to generate the nucleophile specie, which subsequently reacted under stoichiometric control with 4,4’-diformyltriphenylamine **8** in a ratio of 1:1.5 respectively; the yellow oil obtained **9** was fully characterized by spectroscopy methods. The ^{1}H NMR of **9** showed the characteristic signals of the vinyl protons at δ = 7.38 and 6.92 ppm as doublets and *J* = 16.0 Hz, which is distinctive for *E* configuration around the double bond and the signal of the formyl proton at 9.85 ppm; the other signals of this experiment, the ^{13}C NMR data and mass spectrometry confirmed the molecular structure of 9. Our next target became the preparation of the electroactive dyes **Co-D-Ac** and **Co-D-C$_{60}$**; for this purpose we used the (*E*)-4-((4-(4-(dimethyl amine) styryl)phenyl)(phenyl)amino)benzaldehyde **9** as starting material.

In the subsequent step, the dye **Co-D-Ac** was prepared by a Knoevenagel condensation reaction using **9** and cyanoacetic acid **10** in acetonitrile as solvent and pyridine as catalyst, to obtain an orange solid in good yield, this solid showed a band at 2212 cm^{-1} in the IR spectrum due to stretching vibration of de cyano group, in the ^{1}H NMR can be observed the vinyl protons with *E* configuration at $\delta = 7.52$ and 6.72 ppm, additionally the signal of the vinyl proton formed in the reaction is observed at $\delta = 7.85$ ppm. With the aim to prepared the **Co-D-C_{60}** dye we underwent a 1,3-dipolar cyclic addition reaction with *N*-octylglycine and fullerene C_{60} using **9** with the purpose of forming a fulleropyrrolidine group over de buckyball, the reaction was made by heating to reflux in chlorobenzene for a 8h period. Then, a brown solid was obtained from the purification which was characterized. The ^{1}H NMR spectrum of compound **Co-D-C_{60}** shows the characteristic pyrrolidine signature between $\delta = 4.04$ and 4.95 ppm as two doublets (AB system) and one singlet at $\delta = 5.01$ ppm; the other spectroscopy measures confirm the molecular structure of the desired dye.

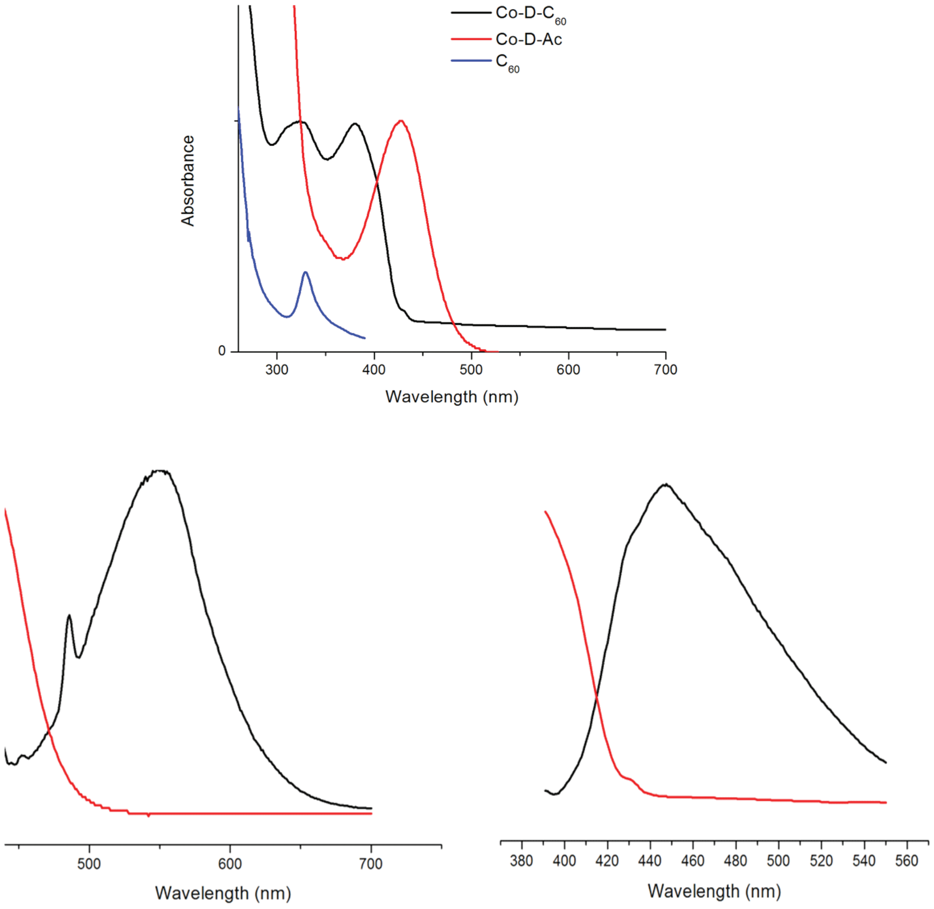


Figure 2. *a) absorption spectrum of* **Co-D-Ac**, **Co-D-C_{60}** *and C_{60}, b) Interception of the absorption and emission spectrum of* **Co-D-Ac**, *c) Interception of the absorption and emission spectrum of* **Co-D-C_{60}**.

UV-vis and emission spectra for compounds Co-D-Ac, Co-D-C_{60} and C_{60} were measured in CH_2Cl_2 as solvent. Interestingly, the absorption bands of Co-D-C_{60}, are a linear combination of the spectra of compound 9 and C_{60}, which indicates that there is not significant electronic communication between both units in the ground-state. Both, absorption and emission spectrum were observed. The intra-molecular charge transfer band at the wavelength red-shifted and the ground-state energy can be calculated by the wavelength of interception of the absorption and emission spectrum (λ_{Int}). These experiments demonstrated favors for push-pull behavior (figure 2). The absorption and emission data are listed in table 1.

Table 1. *Electronic properties data of* **Co-D-Ac** *and* **Co-D-C_{60}** *measured by absorption and emission spectrum.*

	λ_{int} (nm)	λ_{max} (nm)	λ_f (nm)	E_{0-0}/eV	HOMO (eV)	LUMO (eV)
Co-D-C_{60}	415	447	449	2.99	1.04	-1.95
Co-D-Ac	471	549	549	2.64	1.38	-1.26

The electrochemical features of the electro-active compounds **Co-D-Ac** and **Co-D-C_{60}** were studied by cyclic voltammetry using glassy carbon as working electrode; Ag/Ag^+ as reference electrode; Pt as counter-electrode; 0.1 M Bu_4NClO_4, at scan rate of 100 mV/s at room temperature and Fc/Fc^+ as internal reference. Compound **Co-D-C_{60}** shows the reduction profile of three quasi reversible C_{60} reduction waves at potential values for the first reduction wave at -1.18 V, the second and the third waves are appearing at -1.44 V and -1.62 V, respectively (figure 3). As expected, the reduction potential values for **Co-D-C_{60}** are cathodically shifted in comparison with those of pristine C_{60}, which has been accounted for in the saturation of a double bond of the C_{60} sphere which raises the LUMO energy level.

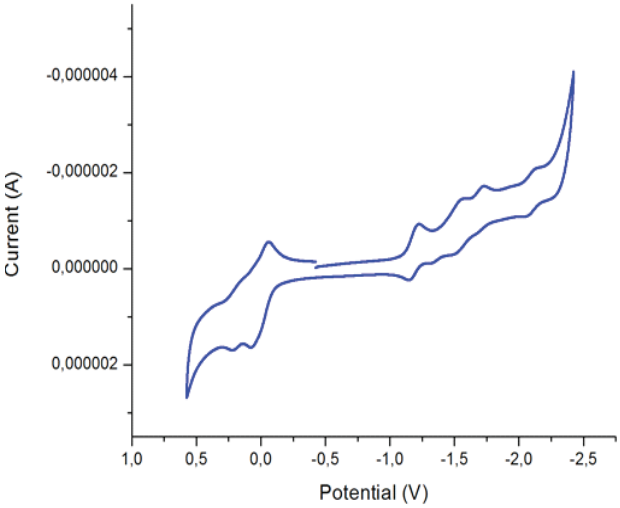
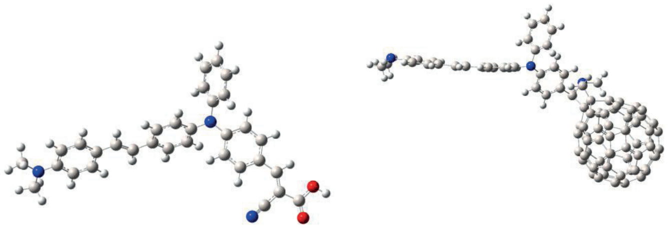


Figure 3. *cyclic voltammogram of the* **Co-D-C_{60}** *with Fc/Fc^+ as internal reference.*

Table 2. *Redox potentials (V) in CH_2Cl_2 of* **Co-D-Ac** *and* **Co-D-C_{60}**

	E_{ox}^{1} (V)	E_{ox}^{2} (V)	$E^{1}_{1/2red}$ (V)	$E^{2}_{1/2red}$ (V)	$E^{3}_{1/2red}$ (V)	$E^{4}_{1/2red}$ (V)
Co-D-C_{60}	0.77	1.28	-1.18	-1.44	-1.62	-2.10
Co-D-Ac	0.75	--	-1.89	--	--	--

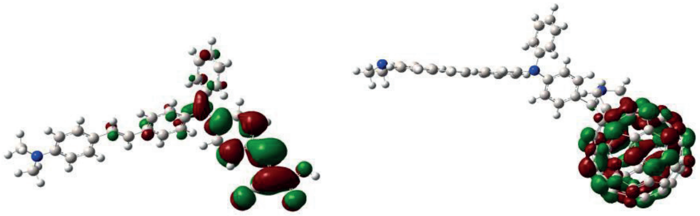
Theoretical calculations at DFT/B3LYP level were carried out in order to gain a better understanding of the electronic structure for dyes **Co-D-Ac** and **Co-D-C_{60}**; and underpinning their experimentally observed push-pull character. The geometry of these dyes was optimized using a 6-21G basis set in the Gaussian 0.9 program [10]. Through the optimized structures calculated of dyes, it can the quasi-planar geometry around of π-conjugated core (figure 4). In frontier orbital analysis, it is evident that the HOMO is mainly localized in the electron–donor moiety mainly in **Co-D-Ac**. As expected, the LUMO is fully localized in the electron–acceptor unit of both dyes (figure 5). The last finding shows a good push-pull behavior for the obtained electroactive systems.



E = -4.1955 x 10^4 eV

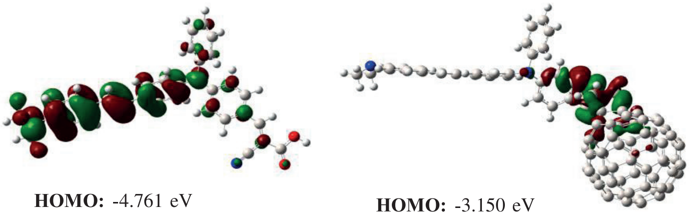
E = -9.8097 x 10^{4} eV

Figure 4. *Minimum-energy conformation calculated for* **Co-D-Ac** *and* **Co-D-C_{60}** *with energy in eV at the B3LYP/3-21G level.*



LUMO: -2.131 eV

LUMO: -0.4269 eV



HOMO: -4.761 eV

HOMO: -3.150 eV

Figure 5. *Electron density contours (0.03 $eBohr^{-3}$) calculated for the HOMO (Bottom) and LUMO (up) of* **Co-D-Ac** *and* **Co-D-C_{60}**.

4 Conclusions

In summary, two novel derivative dyes **Co-D-Ac** and **Co-D-C$_{60}$**, were synthesized using Knoevenagel reactions between (*E*)-4-((4-(4-(dimethyl amine)styryl)phenyl)(phenyl)amino) benzaldehyde **9** and cyanoacetic acid, also using a 1,3-dipolar cycloaddition reaction with *N*-octylglycine and fullerene C$_{60}$ using **9** respectively. The absorption spectra of dyes **Co-D-Ac** and **Co-D-C$_{60}$** exhibit an intra-molecular charge transfer (ICT) band; showed by a broad band in the visible region of the Uv-vis spectra. The emission spectra for **Co-D-Ac** and **Co-D-C$_{60}$** recorded under the same conditions confirmed the ICT band character. The new "push-pull" compounds display a clear electrochemically amphoteric behavior. These findings reveals that there is a significant electronic communication between the electron-codonor-donor units and the electron-acceptor fragment through the π-conjugated core. Finally, a theoretical study performed, confirmed the experimental evidences now reported for the dyes obtained.

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References

[1] Special issue on organic photovoltaics. Acc. Chem. Res.(2009), 42, 1689.

[2] T. Kitamura, M. Ikeda, K. Shigaki, T. Inoue, N. A. Anderson, X. Ai, T. Lian and S. Yanagida, (2004). Phenyl-Conjugated Oligoene Sensitizers for TiO2 Solar Cells. Chem. Mater, 16, 1806.

[3] D. P. Hagberg, T. Edvinsson, T. Marinado, G. Boschloo, A. Hagfeldt and L. Sun, (2006). A Novel Organic Chromophore For Dye-Sensitized Nanostructured Solar Cells. Chem. Commun, 21, 2245.

[4] (a) Z. Ning, Q. Zhang, W. Wu, H. Pei, B. Liu, H. Tian, (2008). Starburst Triarylamine Based Dyes for Efficient Dye-Sensitized Solar Cells. J. Org. Chem, 73, 3791; (b) B. Liu, W. Zhu, Q. Zhang, W. Wu, M. Xu, Z. Ning, Y. Xie, H. Tian,(2009). Conveniently synthesized isophorone dyes for high efficiency dye-sensitized solar cells: tuning photovoltaic performance by structural modification of donor group in donor–π–acceptor system. Chem. Commun, 1766.

[5] T. Marinado, D. P. Hagberg, M. Hedlund, T. Edvinsson, E. M. J. Johansson, G. Boschloo, H. Rensmo, T. Brinck, L. Sun, A. Hagfeldt, (2009). Rhodanine dyes for dye-sensitized solar cells : spectroscopy, energy levels and photovoltaic performance. Phys. Chem. Chem. Phys, 11, 133.

[6] (a) M. Liang, W. Xu, F. Cai, P. Chen, B. Peng, J. Chen and Z. Li, (2007). New Triphenylamine-Based Organic Dyes for Efficient Dye-Sensitized Solar Cells. J. Phys. Chem. C, 111, 4465; (b) W. Xu, B. Peng, J. Chen, M. Liang, F. Cai, (2008). New Triphenylamine-Based Dyes for Dye-Sensitized Solar Cells. J. Phys. Chem. C, 112, 874.

[7] S. Kim, J. K. Lee, S. O. Kang, J. Ko, J. H. Yum, S. Fantacci, F. De Angelis, D. Di Censo, M. K. Nazeeruddin and M. Grätzel, (2006). Molecular Engineering of Organic Sensitizers for Solar Cell Applications. J. Am. Chem. Soc, 128, 16701.

[8] H. Qin, S. Wenger, M. Xu, F. Gao, X. Jing, P. Wang, S. M. Zakeeruddin and M. Grätzel, (2008). An Organic Sensitizer with a Fused Dithienothiophene Unit for Efficient and Stable Dye-Sensitized Solar Cells. J. Am. Chem. Soc, 130, 9202.

[9] (a) S. Komamine, M. Fujitsuka, O. Ito, K. Moriwaki, T. Miyata, T. Ohno, (2000). Photoinduced Charge Separation and Recombination in a Novel Methanofullerene−Triarylamine Dyad Molecule. J. Phys. Chem. A. 104, 11497. (b) F. Gialcone, J. L. Segura, N. Martin, D. M. Guldi, (2004). Exceptionally Small Attenuation Factors in Molecular Wires J. Am.Chem. Soc, 126, 5340. (c) W. Mateusz, J. Santos, B. M. Illescas, A. Ortiz, B. Insuasty, T. Bauer, T. Clark, D. M. Guldi, N. Martin, (2011). Vinyl Spacers—Tuning Electron Transfer Through Fluorene-Based Molecular Wires. Energy Environ. Sci., 4, 765.

[10] Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman Jr JR, et ál. Gaussian 09, Wallingford CT: Gaussian, Inc.; (2010).

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