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Panchromatic Push−Pull Chromophores based on Triphenylamine as Donors for Molecular Solar Cells

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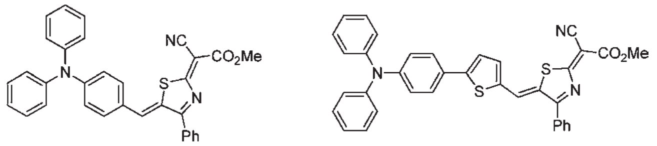
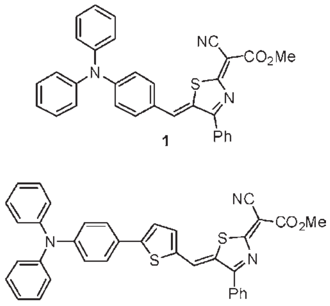
ABSTRACT



Two new push−pull chromophores based on triphenylamine as donor and 2-carboxymethyl-2-cyanomethylenethiazole as acceptor have been synthesized. Both exhibit strong light absorption covering from 300 to 800 nm. Electrochemical studies show HOMO−LUMO gaps of 2.01 and 1.54 eV, making, together with the panchromatic absorption, these systems promising materials in the field of molecular photovoltaic devices.

The conversion of sunlight into electrical energy has activated increasing research in recent years, particularly in organic photovoltaics. In this context, small molecules are an appealing alternative to polymers in bulk heterojunction (BHJ) solar cells, as it has been demonstrated that these systems can be solution processed, achieving efficiencies comparable to polymer systems.[1] Small molecules show several potential advantages including defined structure, easier purification, higher charge mobilities than polymers, and high molecular extinction coefficients. These facts permit limiting the thickness of the active layer or a more straightforward analysis of the relationship between chemical structure and device performance than that for polymers.[2] Among the different classes of material used to this end,[1] push−pull chromophores (an electron donating and an electron withdrawing moiety separated by a π-bridge) are very effective at producing low band gap materials and particularly attractive are molecules based on triphenylamine (TPA),[3] reaching efficiencies up to 2.39%;[4] moreover, introduction of electron acceptor groups in TPA systems leads to the broadening of the absorption spectrum, reduction of the optical gap, and decrease of the HOMO level.[5] In this context, the synthesis of new push−pull dyes based on TPA has shown great potential in the field of molecular photovoltaic devices.[4]



1

2

Figure 1. Structure of the new dyes **1** and **2**.

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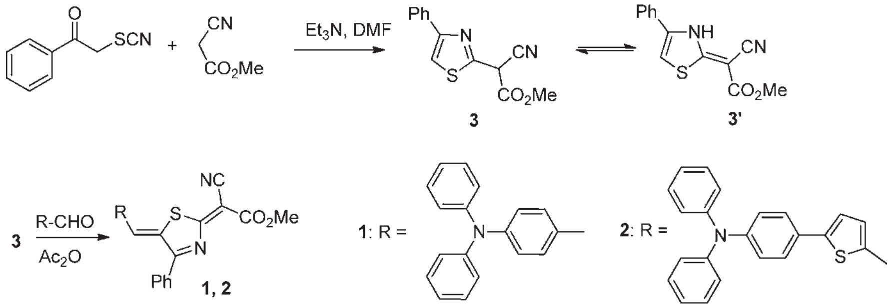
Scheme 1. Synthetic Route to Chromophores **1** and **2**



In this communication we report the synthesis and the optical and electrochemical properties of two new push–pull molecules based on TPA and 2-carboxymethyl-2-cyanomethylenethiazole moiety (Figure 1), with narrow HOMO–LUMO energy gaps, that appear to be promising molecules for molecular bulk heterojunction solar cells.

The synthesis of the two target molecules **1**–**2** was performed according to Scheme 1, starting with the preparation of the thiazole **3** from 2-oxo-2-phenylethylthiocyanate[6] and methylcyanoacetate in 78% yield. Thiazole **3** exists predominantly as its tautomer **3′**, similarly to its analog dicyanomethylene derivative.[7] **1** and **2** were prepared by the acetic anhydride mediated condensation reaction of **3** and **3′** with the commercially available 4-(diphenylamino)benzaldehyde and 5-(4-(diphenylaminophenyl)thiophene-2-aldehyde[8] in moderate yields (58% and 27%, respectively) as dark blue solids.

All compounds were satisfactorily characterized by ^{1}H- and ^{13}C NMR, FT-IR and MALDI-MS spectrometry (see Supporting Information for synthetic details and characterization). Both dyes were unstable in the presence of strong acids when traces of water were present, probably due to a retro-Knoevenagel reaction; otherwise, both dyes were stable.

The optical and electrochemical properties of **1** and **2** have been analyzed by UV–vis absorption spectroscopy, fluorescence emission spectroscopy and cyclic (CV) and Osteryoung (OSWV) voltammetries (Table 1).

The UV–vis absorption spectrum of compound **1**, recorded in dichloromethane (Figure 2 and Table 1), exhibits an intense absorption band in the visible region with maximum at 599.0 nm (log $\varepsilon = 4.61$); on the other hand, compound **2** presents an absorption along the whole visible region, with maximum at 623.0 nm (log $\varepsilon = 4.55$). This bathochromic shift with respect to **1** can be explained by the more extended conjugation due to the presence of the thiophene ring.

When compared with the spectra of the corresponding precursors (the thiazole **3** and the corresponding precursor aldehyde, see Figure S7, Supporting Information), it is clear that these broad absorption bands can be assigned to the intramolecular charge transfer (CT) from the *N*,*N*-diphenylamino moiety (acting as donor) to the methoxycarboxylcyanomethylene substituted thiazole ring (acting as acceptor), behavior that is already observed in related push–pull compounds.[9,10]

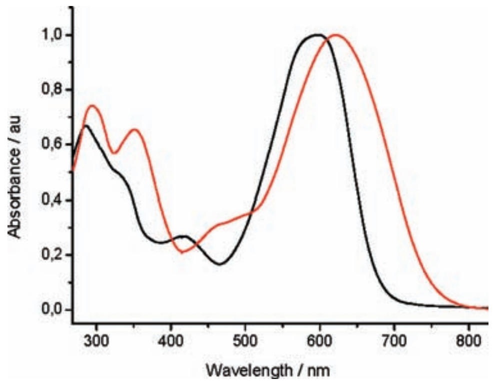


Figure 2. Normalized UV–vis absorption spectra of compounds **1** (black) and **2** (red) in dichloromethane.

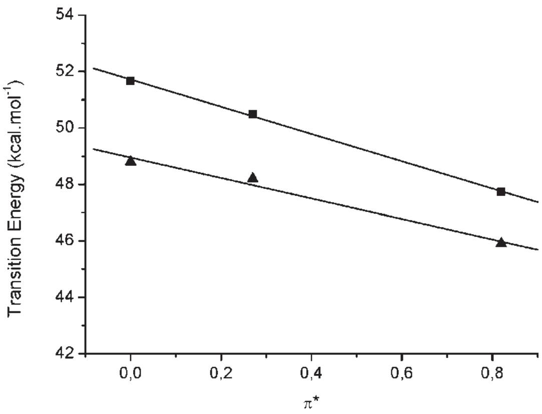


Figure 3. Energy transitions of the low energy band for dyes **1** (■) and **2** (▲) vs Taft constant of solvents.

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Table 1. Data of UV−Vis, Fluorescence Emission Spectroscopies, and OSWV for **1** and **2**

	λ_{max} (nm)[a]	log (ε)[a]	λ_{em} (nm)[b]	E^1_{red} (V)[c]	E^1_{ox} (V)[c]	E_{HOMO} (eV)[d]	ΔE (eV)[e]
1	419−599	3.79−4.61	723.0	−1.26	0.45	−5.25	2.01
2	351−623	4.32−4.55	805.0	−1.17	0.37	−5.17	1.54

[a] 10^{-5} M, in dichloromethane. [b] 10^{-5} M, in dichloromethane, λ_{exc} = 599 nm (**1**) and 623 nm (**2**). [c] [10^{-3} M] in *o*-DCB-acetonitrile (5:1) versus versus Fc/Fc$^+$, glassy carbon, Pt counter electrode, 20 °C, 0.1 M Bu_4NClO_4, scan rate = 100 mV s^{-1}. [d] Calculated respecting to ferrocene, E_{HOMO}: −4.8 eV. [e] Estimated from the difference between E^1_{ox} and E^1_{red}.

For both compounds **1** and **2**, a positive solvatochromism, up to 46 nm for **1** and 37 nm for **2**, is observed by increasing the solvent polarity (Table S1, Supporting Information), confirming the CT character of this band; moreover, we found a good correlation (correlation coeficient >0.99) of the maxima with the Kamlet−Taft π^* constants[11] (Figure 2 and Table S2, Supporting Information). The slope (S) of the Kamlet−Taft equation ($E = E^o + S\pi^*$) is higher, in absolute value, for **1** (S = 4.4) than for **2** (S = 3.6) (Figure 3 and Table S3, Supporting Information), indicating a higher polarizability of **1** and, consequently, better conjugation between the TPA moiety and the 2-carboxymethyl-2-cyanomethylenethiazole acceptor unit.

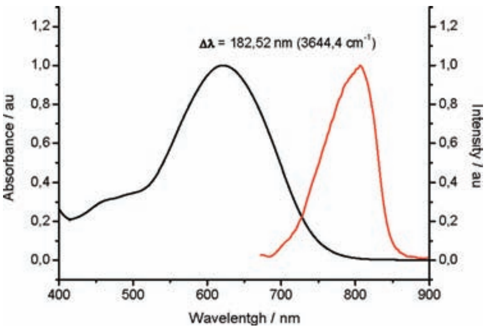

Figure 4. Normalized UV−vis absorption (black) and fluorescence emission (red) spectra of compound **2** in dichloromethane (10^{-5} M) ($\Delta\lambda$ = +182.5 nm).

Fluorescence emission spectroscopy was employed to get information about the excited state-solvent interactions (Figure 4). The results are reported in Table S1 (Supporting Information). Analogously to λ_{max}, the λ_{em} values of **1** and **2** present a large sensitivity to solvent polarity (Figure 5 and Figure S9, Supporting Information). For example, in cyclohexane and dichloromethane, **1** and **2** emit at 681 and 806 nm respectively. This sensitivity to solvent polarity is a characteristic behavior of a photoinduced intramolecular charge transfer. Additionally, the Stokes shift is larger for **2** than for **1** (see Table S1, Supporting Information), suggesting a larger dipolar moment in the excited state than in the ground state.[12]

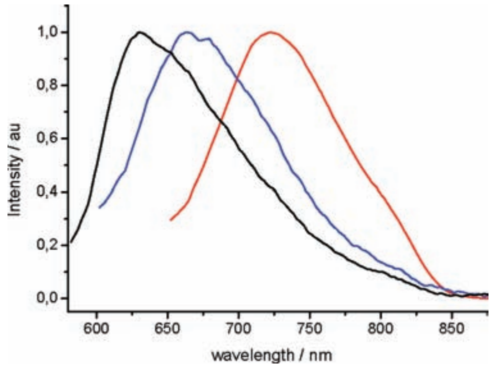

Figure 5. Emission spectra of compound **1** in cyclohexane (black), Diethyl ether (blue) and dichloromethane (red).

The redox properties of **1** and **2** were investigated through CV and OSWV in *o*-dichlorobenzene-acetonitrile (4:1), (Table 1, Figures S10 and S11, Supporting Information). In the cathodic side, both compounds show a first reversible oxidation wave (at 0.45 V (**1**) and 0.37 V (**2**) vs Fc/Fc$^+$), assigned to the TPA moiety (this assignment is consistent with the oxidation potential of TPA-CHO). For compound **2**, the conjugation of the TPA with the thiophene group lead to a decrease of the E_{ox} value by 60 mV respective to **1**. A second irreversible oxidation wave is observed at 0.80 V for **2**. On the reduction side, both compounds show an irreversible wave at 1.26 V (**1**) and 1.17 V (**2**). The E_{HOMO} values (calculated with respect to ferrocene as reference, E_{HOMO}: −4.8 eV[13]) were determined as −5.25 eV for **1** and −5.17 eV for **2**. The HOMO−LUMO gaps, electrochemically determined, are as narrow as 2.01 and 1.54 eV, respectively; these values illustrate that the interest of these materials, as a low energy gap, together

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with low-lying LUMO level, appears to be the route to higher efficiency organic solar cells.[14]

The structures of **1** and **2** have been optimized using DFT-B3LYP 6-31G with Gaussian 03W. The π-system is almost coplanar as the dihedral angles between the aminophenyl group (in **1**) or the thiophene (in **2**) and the thiazole ring are 6.9° and 5.6°, respectively. The dihedral angle between the aminophenyl group and the thiophene (in **2**) is 15.5°; moreover, the bond distances thiophene–methine and methine–thiazole in **1** (Figure 6, top) differ only by $\sim$0.05 Å, suggesting the partially quinoid character. These angles and distances are similar to the data afforded by X-ray crystallography study in related compounds,[10b] confirming the intramolecular charge transfer (*vide supra*).

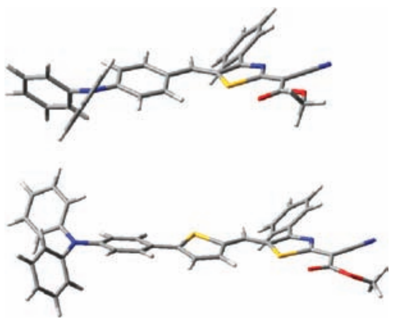

Figure 6. Geometry of compounds **1** (top) and **2** (bottom) optimized with Gaussian 03W at the DFT-B3LYP 6-31G level of theory.

As expected, the HOMO is delocalized along the π-conjugated system with an important contribution of the TPA while the LUMO is mainly located on the 2-carboxymethyl-2-cyanomethylenethiazole moiety. Thus, the HOMO to LUMO electronic transition has a strong intramolecular charge transfer character. The calculated HOMO and LUMO energies in the gas phase are −5.33 and −2.97 eV for compound **1** (Figure S12, Supporting Information) and 5.25 and −3.21 eV for compound **2** (Figure S13, Supporting Information).

In conclusion, two new push–pull chromophores based on triphenylamine as donor and 2-carboxymethyl-2-cyanomethylenethiazole as acceptor have been synthesized. These compounds exhibit strong panchromatic absorption in the visible spectrum and show some absorption in the near-infrared region due to the existence of charge transfer bands; these molecules show positive solvatochromism with a good correlation between the energy of the transition and the Kamlet–Taft π^* constants. Electrochemical studies show HOMO–LUMO gaps as low as 2.01 and 1.54 eV, respectively, making these systems, together with the broad absorption on the visible region, promising materials in the field of molecular photovoltaic devices. Moreover, the hydrolysis of the ester group can, in the future, afford interesting materials as photosentitizers attached to TiO_2 in dye sensitized solar cells (DSSC). The synthesis of new members of this family of compounds as well as investigations on the photovoltaic properties of these noticiable materials is in progress.

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Supporting Information Available. Synthetic procedures and characterization for new compounds, including ^{1}H NMR, ^{13}C NMR and MALDI-TOF spectra. UV–vis and fluorescence spectra, Taft constants of solvents and molecular orbitals for **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.