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Optical properties of donor-π-(acceptor)$_n$ merocyanine dyes with dicyanovinylindane as acceptor group and triphenylamine as donor unit

Xiaochuan Li [a,b], Sung-Hoon Kim [c], Young-A. Son [a,*]

[a] *School of Chemical and Biological Engineering, Chungnam National University, Daejeon 305-764, South Korea*
[b] *College of Chemistry and Environmental Science, Henan Normal University, Xinxiang, Henan 453007, China*
[c] *Department of Textile System Engineering, Kyungpook National University, Daegu 702-701, South Korea*

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ABSTRACT

Donor-π–(Acceptor)$_n$ (D-π-A) type dyes were synthesized and their absorption and emission spectra investigated in different solvents. Strong acceptor units imparted large red-shifts in absorption; the twisting of the dye's structure imposed by an acceptor unit quenched fluorescence. Electron delocalization before and after excitation was observed according to molecular orbital calculations. The results indicated potential use of the dyes as electro-optical materials.

1. Introduction

Donor–acceptor-substituted chromophores are the most important class of compounds for elucidating the relationships between push–pull chromophores and their optical properties [1]. The best-known dyes of this kind are Brooker's dye with negative solvatochromism and, in particular, Reichardt's dye with its pronounced positive solvatochromism [2]. Despite the broad application of these and other donor-π-acceptor (D-π-A) chromophores [3,4] for the elucidation of reaction rates, chemical equilibria, nonlinear optical properties, and so on, accurately explaining the relationship between substituted groups and optical properties remains the subject of active debate [5]. Thus, while it is nowadays well accepted that the magnitude of the energy difference between the ground and excited states of a dipolar dye is significantly influenced by the intermolecular, solute–solvent interactions, there is no consensus on the extent to which the ground-state molecular structure of the dye is modified by polarization produced by a polar solvent.

Depending on the donor and acceptor strengths of the terminal groups, the electronic structure of merocyanines in the ground-state changes from a polyene-like type structure (**A**) through a fully delocalized cyanine type (**B**) to a zwitterionic structure (**C**) (Fig. 1). The length of the polymethine chain and its flexibility are also of considerable importance in determining their specific properties [6].

The synthesis of merocyanines with the desired characteristics is one of the most challenging areas in cyanine chemistry. Much effort has been focused on the search for new preparative variants and reagents for synthesis. The insertion of new or specifically substituted heterocyclic ring systems and the synthesis of dyes with specific substituents in the polymethine chain are also important points [6].

In recent years, this model with interdependent ground and excited states has been applied to evaluate D-π-A chromophores for nonlinear optics [7]. Although the donor and acceptor strengths and the influence of the π-conjugated bridge have been experimentally

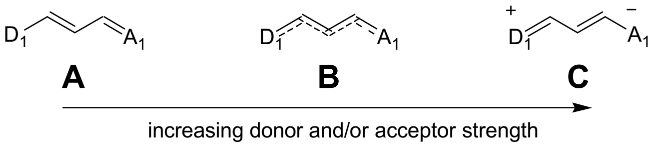

Fig. 1. Electronic structures of merocyanines.

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* Corresponding author. Tel.: +82 42 821 7694; fax: +82 42 823 3736.
E-mail address: yason@cnu.ac.kr (Y.-A. Son).

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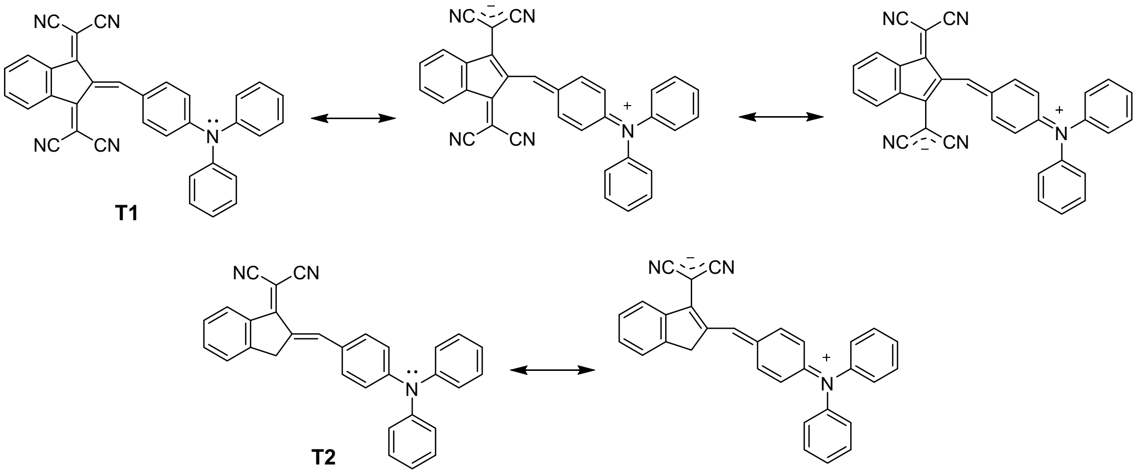


Scheme 1. π-Charge distribution in target D-π-A dyes according to a simple model.

addressed in great detail, it is necessary to get deeper insight into the relationship between the donor/acceptor strengths and the spectral properties. With this in mind, two novel merocyanine dyes were designed that were structurally related but supposed and predicted to show different optical properties. Strong acceptor units, 1,3-bisdicyanovinylindane and 1-dicyanovinylindane, were incorporated onto triphenylamine, a stronger donor unit. The structures of the dyes were altered by dipolar solvents between two or three limiting mesomeric structures, a nonpolar and a zwitterionic one (Scheme 1).

2. Experimental

2.1. Materials

Solvents used in photochemical measurements were of spectroscopic grade and were purified by distillation before use. NMR spectra were recorded on an NMR spectrometer JEOL-AL400 operating at 400 (^{1}H) and 75 MHz (^{13}C) with chemical shifts referenced to internal Me_4Si (TMS). Mass spectra were measured with a mass spectrometer LC–MS (Waters120 QTof). Absorption spectra were measured with an Agilent 8453 spectrophotometer. Fluorescence spectra were measured on a SHIMADZU RF-5301PC fluorescence spectrophotometer.

2.2. Electrochemical measurements

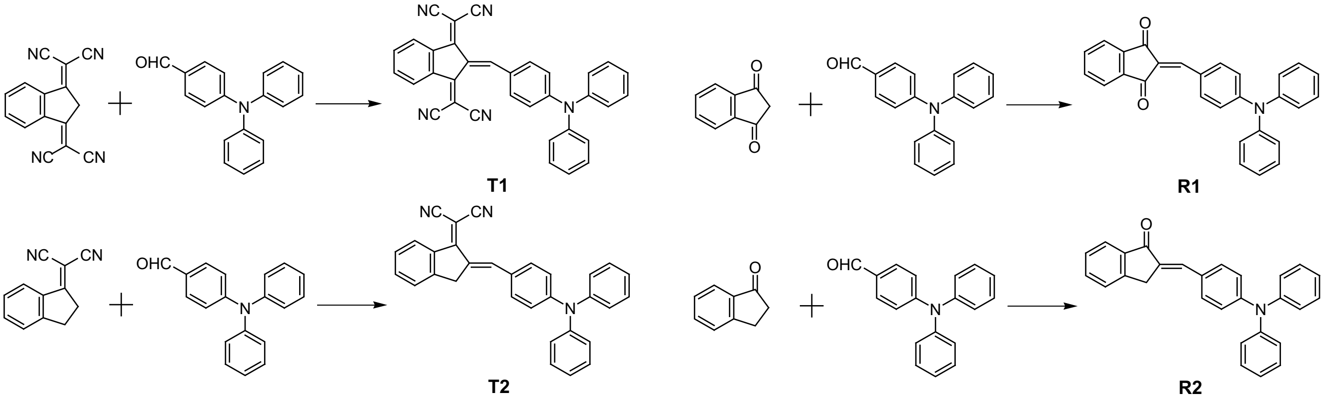
Cyclic-voltammetric measurements were carried out in a conventional three-electrode cell using a Platinum button working electrode of 2 mm diameter, a platinum-wire counter electrode, and an Ag/AgCl reference electrode on a computer-controlled VersaStat 3 model V3 at room temperature. A 0.1 M solution of tetrabutylammonium hexafluorophosphate ($TBAPF_6$) was used as supporting electrolyte and the scan rate was set to 100 mV/s. The energy levels were calculated using the ferrocene (E_{FOC}) value of −4.8 eV as the standard. In this report, we used the ionization potential converted from oxidation potentials for the comparison of the energies of the highest occupied molecular orbital (HOMO).

2.3. Preparation and characterization

As presented in Scheme 2, two merocyanines dyes were synthesized by conventional condensation (**T1** and **T2**). For comparison of the optical properties, two reference compounds (**R1** and **R2**) were also synthesized according to literature methods with some modifications [8–13].

2.3.1. Target compound **1** (**T1**)

121 mg (0.5 mmol) of 1,3-bisdicyanovinylindane [14] and 150 mg (0.55 mmol) of 4-formyltriphenylamine were dissolved in



Scheme 2. Synthetic routes for target and reference compounds.

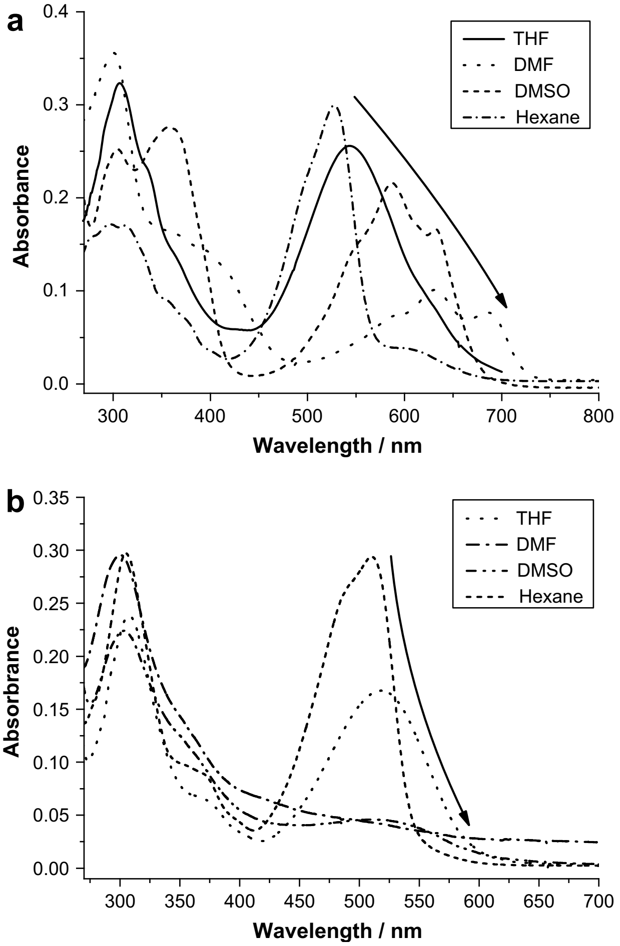


Fig. 2. Absorption spectra of **T1** (a) and **T2** (b).

10 mL of acetic anhydride. The mixture was then heated to 60 °C for 4 h. The solvent was evaporated in vacuum. The residue was purified by column chromatography (ethyl acetate/hexane, 1/4, v/v) to give 100 mg of pure **T1** (40% yield).

^{1}H NMR(CD_3COCD_3): 8.55 (m, 3H); 8.00 (m, 2H); 7.69 (d, J = 8.8 Hz, 2H); 7.47–7.43 (t, J = 8.3 Hz, J = 7.5 Hz, 4H); 7.29–7.24 (m, 6H); 7.00 (d, J = 9.0 Hz, 2H). ^{13}C NMR (CD_3COCD_3): 162.6, 153.1, 146.7, 144.3, 135.4, 134.5, 130.8, 129.6, 127.3, 126.7, 126.6, 126.2, 120.3, 114.7, 114.3. MS m/z: 497 (M^+). Anal. Cald. for $C_{34}H_{19}N_5$: C, 82.08; H, 3.85; N, 14.08; Found: C, 82.05; H, 3.90; N, 14.04%.

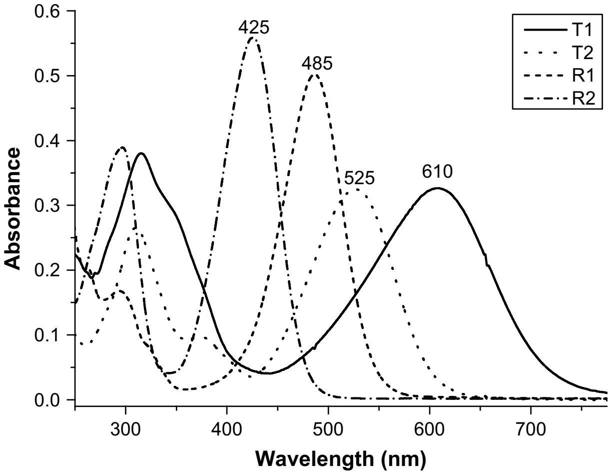


Fig. 3. Absorption spectra of **T1**, **T2**, **R1**, and **R2** in dichloromethane.

2.3.2. *Target compound **2** (**T2**)*

180 mg (1 mmol) of 1-dicyanovinylindane [15], 273 mg (1 mmol) of 4-formyltriphenylamine and several drops of piperidine were dissolved in 15 mL of toluene. The mixture was refluxed for 3 h. The solvent was then evaporated in vacuum. The residue was purified by column chromatography (CH_2Cl_2/hexane, 3/2, v/v) to give 240 mg of pure **T2** (55% yield).

^{1}H NMR (CD_3COCD_3): 8.53 (d, J = 8.0 Hz, 1H); 8.29 (s, 1H); 7.71 (m, 4H); 7.57–7.54 (m, 1H); 7.44–7.40 (m, 4H); 7.23–7.20 (m, 6H); 7.05 (d, J = 8.8 Hz, 2H), 4.15 (s, 2H). ^{13}C NMR (CD_3COCD_3): 167.9, 151.1, 148.9, 147.3, 137.8, 137.5, 135.1, 135.0, 133.6, 130.7, 128.8, 128.5, 126.9, 126.6, 125.9, 125.8, 121.1, 116.7, 116.3, 67.4, 38.1. MS m/z: 435 (M^+). Anal. Cald. for $C_{31}H_{21}N_3$: C, 85.49; H, 4.86; N, 9.65; Found: C, 85.53; H, 4.90; N, 9.68%.

2.3.3. *Reference compound **1** (**R1**)*

205 mg (1.4 mmol) of 1,3-indanedione and 382 mg (1.4 mmol) of 4-formyltriphenylamine were dissolved in 15 mL of butan-1-ol and refluxed for 2 h. Then the mixture was cooled to room temperature. The solid precipitate was collected and recrystallized from n-butanol to give 455 mg of pure compound (78% yield).

^{1}H NMR ($CDCl_3$): 8.42 (d, J = 9.0 Hz, 2H); 7.97–7.93 (m, 2H); 7.78–7.73 (m, 3H); 7.38–7.34 (m, 4H); 7.22–7.18 (m, 6H); 7.02 (d, J = 9.5 Hz, 2H). ^{13}C NMR ($CDCl_3$): 191.3, 189.6, 152.7, 146.6, 145.7,

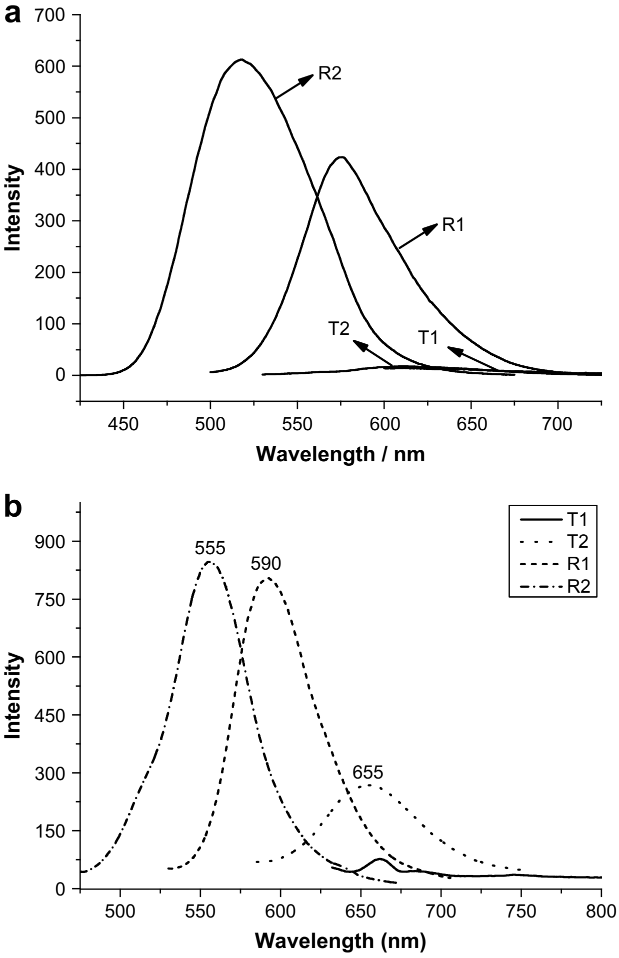


Fig. 4. Emission spectra of **T1**, **T2**, **R1**, and **R2** in THF (a) and in the solid state (b).

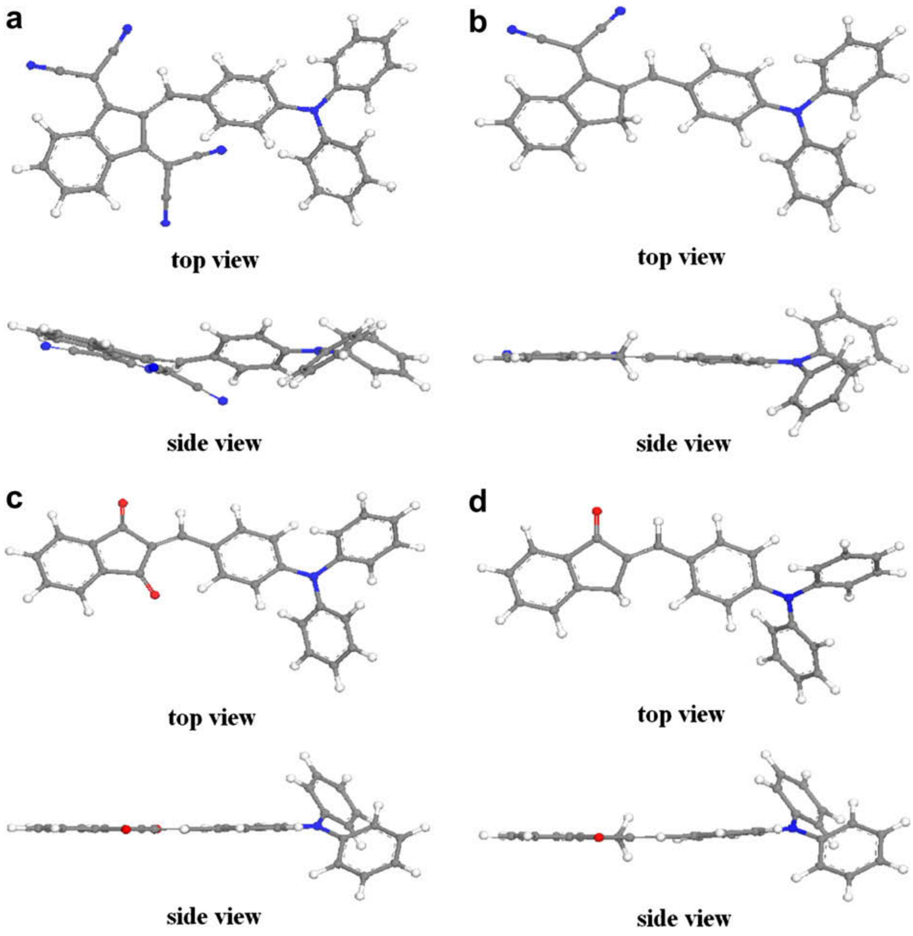


Fig. 5. Calculated geometry structures of **T1** (a), **T2** (b), **R1** (c), and **R2** (d) using the MS package suite program with BLYP/GGA basis sets.

142.3, 139.9, 136.8, 134.7, 134.5, 129.7, 126.5, 125.7, 125.5, 125.5, 122.8, 122.7, 118.8. MS *m*/*z*: 401 (M^+). Anal. Cald. for $C_{28}H_{19}NO_2$: C, 83.77; H, 4.77; N, 3.49; Found: C, 83.73; H, 4.81; N, 3.51%.

2.3.4. Reference compound *2* (*R2*)

A solution of 132 mg (1.0 mmol) of 1-indanone in 15 mL of dry methanol was added to 287 mg (1.05 mmol) of 4-formyltriphenylamine and 18 mg of NaOMe in 7 mL of dry methanol. The mixture was stirred at room temperature while the color was changed from brown to bright yellow. After the reaction was completed, as determined by TLC monitoring, the solution was evaporated under vacuum and the residue was purified by column chromatography (EtOA/hexane, 1/20, v/v) to give 150 mg of pure **R2** (39% yield).

^{1}H NMR (CD_3COCD_3): 7.78 (d, $J = 7.6$ Hz, 1H); 7.71–7.64 (m, 4H); 7.49 (t, $J = 8.8$ Hz, $J = 5.8$ Hz, 2H); 7.40–7.37 (t, $J = 7.4$ Hz, $J = 8.4$ Hz, 4H); 7.16–7.12 (m, 6H); 6.97 (s, $J = 8.8$ Hz, 2H), 4.07 (s, 2H). ^{13}C NMR ($CDCl_3$): 194.2, 149.3, 149.2, 146.7, 138.3, 134.1, 133.8, 132.1, 132.0, 129.4, 128.2, 127.4, 126.0, 125.4, 124.2, 124.1, 121.3, 32.5. MS *m*/*z*: 387 (M^+). Anal. Cald. for $C_{28}H_{21}NO$: C, 86.79; H, 5.46; N, 3.61; Found: C, 86.75; H, 5.49; N, 3.58%.

3. Results and discussion

The synthesis proceeded by the condensation 4-formyltriphenylamine with different indanone derivatives, while different solvents and bases were applied for their condensation. From **T1**, **T2**, **R1**, to **R2**, the solvent was varied from acetic anhydride, toluene, butan-1-ol, to methanol. The condensation between 4-formyltriphenylamine and 1,3-indanedione or 1,3-bisdicyanovinylindane could be effected smoothly without the presence of base. However, the condensation between 4-formyltriphenylamine and 1-indanone or 1-dicyanovinylindane must be carried out with the presence of base. All the four compounds were obtained with moderate yield.

Both **T1** and **T2** are stable and dissolved adequately in common organic solvents such as hexane, dichloromethane (DCM), tetrahydrofuran (THF), *N*,*N*-dimethylformamide (DMF), and dimethyl sulfoxide (DMSO). **T1** exhibited an obvious solvatochromic shift from nonpolar hexane to polar DMSO in the π–π^* absorption band from 527 to 687 nm, respectively. However, the solvatochromic shift for **T2** (510–530 nm) was smaller than that of **T1** (Fig. 2b). It is known that solvatochromism depends on the molecular structure, the nature of the chromophore, as well as the solvents [3].

Generally, the positive solvatochromism with increasing solvent polarity indicates that the dipole moment of the molecule in the excited state (μ_e) is expected to be higher than that of the ground state (μ_g). The μ_e of **T1** and **T2** should be higher than their μ_g. The absorption in DCM was different from other solvents. Fig. 3 shows the absorption spectrum of **T1** extended to 610 nm which is larger than **T2**, **R1**, and **R2**. The introduction of malononitrile moieties caused a dramatic shift to longer wavelengths in DCM.

The fluorescence spectra of **T1** and **T2** were very weak in THF, while **R1** and **R2** exhibited strong fluorescence in THF (Fig. 4a). As the number of the acceptor units on the dye molecule increased, the intramolecular repulsion increased, which caused a molecular

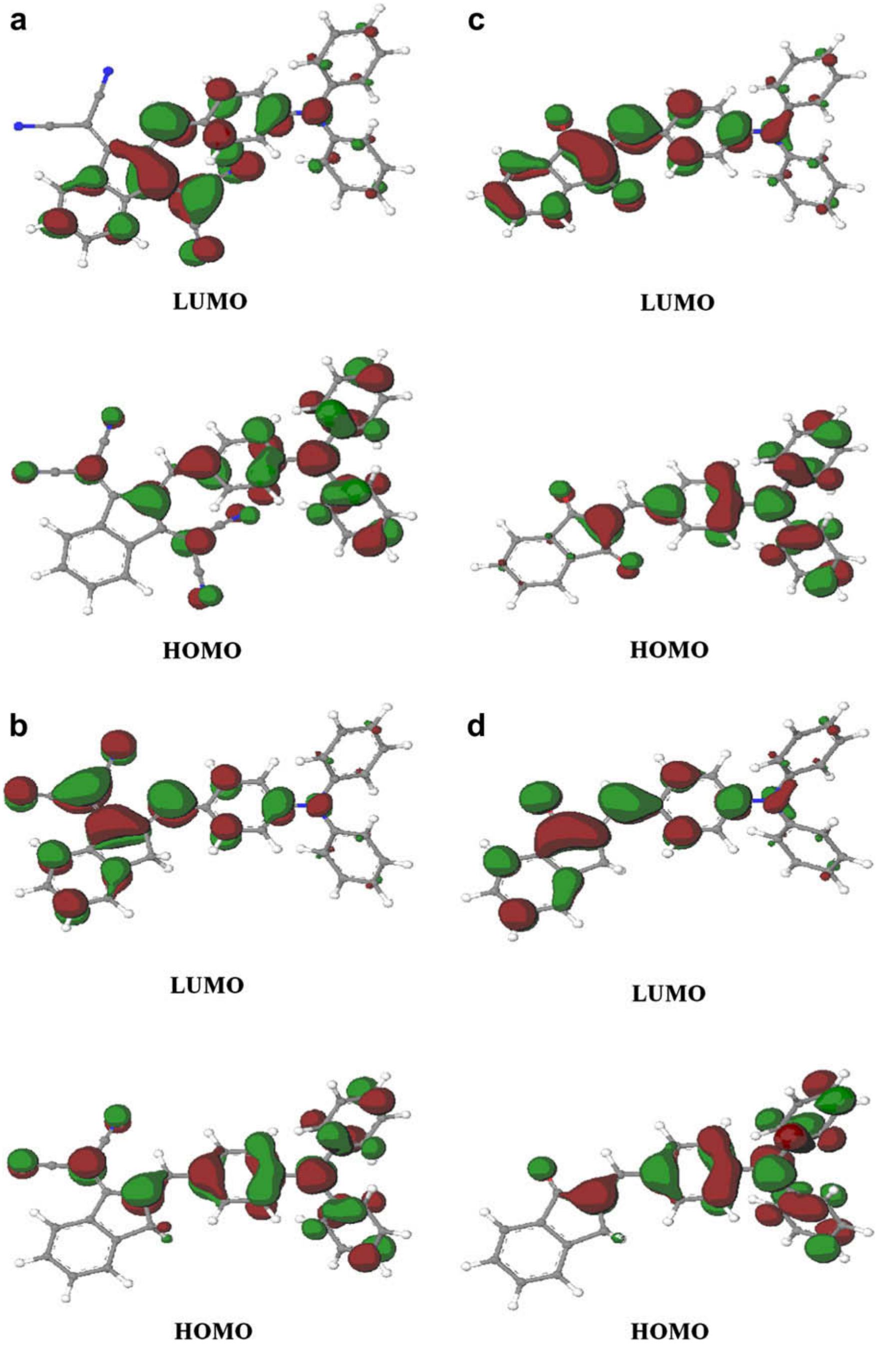


Fig. 6. Diagrams showing the HOMO and LUMO levels of **T1** (a), **T2** (b), **R1** (c), and **R2** (d).

twist, loss of π-conjugation, and loss of fluorescence. This effect of added malononitrile moieties on the properties of these dyes was further verified by their emission spectra in the solid state (Fig. 4b), which also exhibited a dramatic shift in the solid state emissions to longer wavelengths.

For deeper understanding of spectra and electron properties displayed by **T1** and **T2**, the geometrical structure and molecular orbital calculations for one density functional (DFT) level of these dyes were performed using a BLYP/GGA basis set, employing Material Studio (MS) suite of programs. The calculations revealed that the **T1** was highly twisted because of steric hindrance between the cyano moiety and the benzene rings, which is in accordance with the results of emission studies (Fig. 5). However, **T2** was a conjugated molecule through double bond. For **R1** and **R2**, molecules were well conjugated with the spacer and benzene ring, which was enhanced by intramolecular interactions between the oxygen atom and corresponding hydrogen atoms. The introduction of strong acceptor units caused red-shift of the absorption and emission wavelengths, but the fluorescence intensity was quenched by the twisted molecular structure. The molecular orbital calculations revealed that the electron density in the HOMO of these compounds was mainly distributed over the donor groups before excitation, and the electron was delocalized to the acceptor groups after excitation (Fig. 6). According to Fig. 5, a more effective excited-state intramolecular charge transfer (ICT) from triphenylamine moiety to indandione moiety was suggested in these

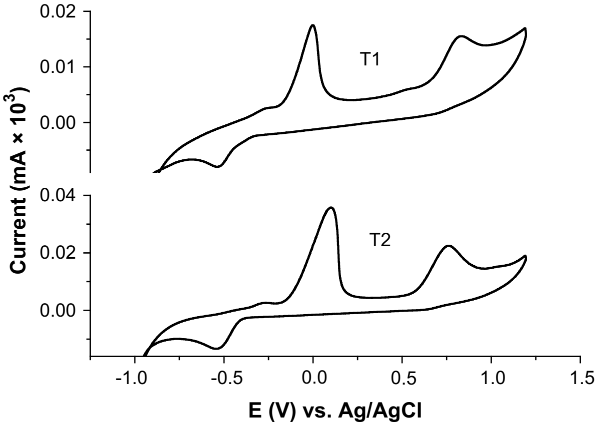


Fig. 7. Cyclic voltammograms of **T1** and **T2** measured in CH_3CN solution containing 0.1 M $TBPAF_6$ at 20 °C.

compounds. These results exhibit the typical push–pull characteristic of the D-π-A type molecules.

The electronic states (HOMO/LUMO) of **T1** and **T2** were investigated by cyclic voltammetry (CV). As shown in Fig. 7, **T1** and **T2** both exhibited oxidation and reduction peaks. The estimated electron affinity (EA, LUMO level) values for **T1** and **T2** were −3.85 eV and −3.84 eV, respectively. Although there is a difference in the molecular structure, the electron distribution in LUMO is similar. Electrons were located on one of the dicyanoethylene unit. For comparison, the electronic states of reference compounds (**R1** and **R2**) were tested. It showed that the LUMO values of the two compounds were lower than for **R1** (−3.68 eV) and **R2** (−3.76 eV), respectively and considerably lower than the most popular electron-transport material, Alq_3 (−3.0 eV) [16]. The ionization potential (IP, HOMO level) of **T1** and **T2** were −5.21 eV and −5.14 eV, respectively. One more dicyanoethylene enhanced the acceptor strength, which resulted that the HOMO of T1 was slightly more stable than that of T2. The superior electron-accepting features of these compounds make them very promising as charge-transport materials in practical applications.

4. Conclusions

Two Donor-π–(Acceptor)$_n$ type dyes and two reference compounds were synthesized and their optical properties investigated; their optimized geometric structures and molecular orbitals were calculated. The experimental results confirmed the predicted properties of the dyes and offered reasonable explanations for their optical properties. The introduction of strong acceptor units to the D-π-A system caused a dramatic 125 nm spectral red-shift to 610 nm. The ensuing, highly twisted molecular structure quenched fluorescence both in solution and in the solid state.

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