Journal of Photochemistry and Photobiology A: Chemistry 251 (2013) 1–9

Contents lists available at SciVerse ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

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

Tuning photophysical properties of triphenylamine and aromatic cyano conjugate-based wavelength-shifting compounds by manipulating intramolecular charge transfer strength

Yilin Li[a,b], Tianhui Ren[a,*], Wen-Ji Dong[b,**]

[a] School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, Shanghai 200240, China
[b] Voiland School of Chemical Engineering and Bioengineering, Washington State University, Pullman, WA 99164, USA

ARTICLE INFO

Article history:
Received 11 June 2012
Received in revised form 28 August 2012
Accepted 2 October 2012
Available online 17 October 2012

Keywords:
Triphenylamine
Wavelength-shifting materials
Large Stokes shift
ICT
DFT

ABSTRACT

A series of triphenylamine-based aromatic cyano compounds have been synthesized as red-emitting fluorophores with large Stokes shifts in both solution (>100 nm in $CHCl_3$) and solid state (>150 nm in film). Intramolecular charge transfer (ICT) properties of the synthesized compounds are examined using UV–Vis absorptions, photoluminescence measurements and solvatochromic studies. Our studies suggest that Stokes shifts of these compounds can be fine-tuned by manipulating the ICT strength between donor and acceptor with various electronic donating groups, and the largest Stokes shifts are typically associated with compounds that have the strong ICT characters. The observed spectroscopic properties of the compounds are consistent with theoretical calculations using density function theory (DFT) or time-dependent density function theory (TD-DFT). The calculations suggest that the ICT occurs from localized HOMO to localized LUMO with magnitudes of 60–80%. The relative quantum yields of these fluorophores in solution are various and highly solvent dependent. In solid state, the quantum yields of the compounds are significantly increased and some can reach to 0.40.

1. Introduction

Organic π-conjugated compounds have been extensively explored as the photonic-related materials in many disciplines of science due to their special photophysical properties of light absorption and emission. In this process, photons are absorbed and re-emitted, which results in the occurrence of energy relaxation from high energy wavelength to low energy wavelength. Therefore, these materials have wide applications including organic field-effect transistors [1], organic light-emitting diodes [2], organic photovoltaics [3–5] and biochemical sensors [6]. On the other hand, these π-conjugated compounds can also be used as wavelength-shifting materials to improve performance of cadmium telluride (CdTe) solar cells. It is known that CdTe solar cells have poor response efficiency (<20%) to the light under 500 nm. To improve the light response under 500 nm of the solar cells, a layer of wavelength-shifting materials, which absorb the light under 500 nm and re-emit light at more favorable wavelength (>550 nm), can be placed on the surface of the solar cells [7].

It is well known that anthracene [8], pyrene [9] and perylene [10] derivatives show high light-emitting performance due to their high quantum yields and have been widely used to develop new optical devices. However, small Stokes shifts (<25 nm) are typically associated with these types of materials, which can lead to serious self-quenching [11] and constrain the full potential of their applications. To enlarge the Stokes shift of these materials and eliminate the mentioned weakness in their applications, one possible solution is to create a Förster resonance energy transfer (FRET) system, which contains donor and acceptor molecules [12]. In this system, emission at a longer wavelength can be achieved by the emission of acceptor, which gets the excitation energy from the absorption of the donor at short wavelength – the pseudo Stokes shift is typically over 50 nm. However, this design requires a spectral overlap between the donor emission and the acceptor absorption as well as the adequate distance between them. More importantly, parallel alignment of the dipole moments of the donor and acceptor is required to reduce the energy loss caused by fluorescence anisotropy. To avoid these constrain associated with the FRET system, new approaches are needed to design new fluorophores with large Stokes shift and other optimal photophysical properties such as high quantum yields. It is found recently that compounds with strong intramolecular charge transfer (ICT) properties show large Stokes shifts based on the theory of Lippert and Mataga [13,14]. Large Stokes shift has been achieved in organic fluorophores

---

* Corresponding author. Tel.: +86 21 54747118.
** Corresponding author. Tel.: +1 509 335 5798.
E-mail addresses: thren@sjtu.edu.cn (T. Ren), wdong@vetmed.wsu.edu (W.-J. Dong).

1010-6030/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jphotochem.2012.10.002

consisting of electron donating and accepting parts with the increase of conjugation bridge length [15]. However the intermolecular aggregation due to the long chains of these fluorophores can significantly reduce their energy conversion efficiency [16]. It has also noticed that stronger electron-withdrawing groups attached to the acceptor increase the ICT character of the fluorophore [17], therefore, different electron-withdrawing groups can be used to tuning the ICT character [18].

Here, we reported a study on tuning the ICT properties of a series of triphenylamine-based aromatic cyano compounds by manipulation the conjugation and strength of different donors and acceptors of the compounds. Strong ICT character (near 80% theoretically) accompanied by large Stokes shifts (over 100 nm in $CHCl_3$) and quantum yields up to 0.19 in $CHCl_3$ and 0.73 in 1,4-dioxane were observed with these synthesized red-emitting fluorophores. Properties of these compounds in solid state are also studied. The quantum yield in solid state is estimated up to 0.40. Potentially, these red-emitting fluorophores may find applications in wavelength-shifting materials for enhancement of the efficiency of some man-made solar cells.

2. Experimental

2.1. General methods

All reagents were used as received and without further purification. Chromatographic purification was carried out with 60-200 mesh silica gel for flash columns. Final compounds were characterized by ^{1}H NMR, ^{13}C NMR, MALDI-MS and elemental analysis (C, H, N percentage) to prove the purity for the spectroscopic measurements.

2.2. Spectroscopic measurements

Absorption spectra were recorded with a Bechman Coulter DU730 Life Science UV–Vis spectrophotometer at room temperature. Emission spectra from 200 nm to 800 nm were collected on an ISS PC1 photon counting spectrofluorometer at 20 °C. Fluorescence lifetimes were measured on a HORIBA JOBIN YVON fluorocube using 459 nm LED as the excitation light source.

2.3. Computational methods

All calculations were conducted by using the Gaussian 09 package [19].

2.4. Compounds characterization

2.4.1. 2-((4′-(Diphenylamino)biphenyl-4-yl)methylene)malononitrile (**1a**)

Red solid (yield 11%). $R_f = 0.43$ (Hex:EtOAc = 3:1). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.97 (d, 2H, $J = 8.5$ Hz), 7.75 (s, 1H), 7.73 (d, 2H, $J = 8.7$ Hz), 7.54 (d, 2H, $J = 8.8$ Hz), 7.31 (t, 4H), 7.18-7.08 (m, 8H). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 159.4, 149.2, 147.3, 147.0, 131.8, 131.7, 129.7, 129.4, 128.2, 127.3, 125.4, 124.0, 122.9, 114.4, 113.3, 81.2. MALDI-MS: m/z calcd for $C_{28}H_{19}N_3^+$ 397.1579, found 397.0719. Anal. (%): calcd (found) for $C_{28}H_{19}N_3$: C 84.61 (84.58), H 4.82 (4.18), N 10.57 (10.44).

2.4.2. 2-((4′-(Dip-tolylamino)biphenyl-4-yl)methylene)malononitrile (**1b**)

Red solid (yield 26%). $R_f = 0.20$ (Hex:EtOAc = 10:1). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.95 (d, 2H, $J = 8.5$ Hz), 7.74 (s, 1H), 7.71 (d, 2H, $J = 8.6$ Hz), 7.49 (d, 2H, $J = 8.9$ Hz), 7.13-7.04 (m, 10H), 2.34 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 159.4, 149.6, 147.2, 144.7, 133.9, 131.8, 130.7, 130.3, 129.2, 128.0, 127.1, 125.6, 121.6, 114.5, 113.3, 80.9, 21.1. MALDI-MS: m/z calcd for $C_{30}H_{23}N_3^+$ 425.1892, found 425.2034. Anal. (%): calcd (found) for $C_{30}H_{23}N_3$: C 84.68 (84.25), H 5.45 (4.99), N 9.87 (9.78).

2.4.3. 2-((4′-(Bis(4-methoxyphenyl)amino)biphenyl-4-yl)methylene)malononitrile (**1c**)

Black solid (yield 14%). $R_f = 0.31$ (Hex:EtOAc = 3:1). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.94 (d, 2H, $J = 8.6$ Hz), 7.73 (s, 1H), 7.70 (d, 2H, $J = 8.6$ Hz), 7.48 (d, 2H, $J = 8.9$ Hz), 7.11 (d, 4H, $J = 9.0$ Hz), 6.97 (d, 2H, $J = 8.8$ Hz), 6.87 (d, 4H, $J = 9.0$ Hz), 3.82 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 159.3, 156.7, 150.1, 147.2, 140.2, 131.8, 129.6, 129.0, 128.0, 127.5, 127.0, 119.7, 115.1, 114.5, 113.4, 80.7, 55.7. MALDI-MS: m/z calcd for $C_{30}H_{23}N_3O_2^+$ 457.1790, found 425.2006. Anal. (%): calcd (found) for $C_{30}H_{23}N_3O_2$: C 78.75 (78.63), H 5.07 (4.91), N 9.18 (8.91).

2.4.4. 2-((5-(4-(Diphenylamino)phenyl)thiophen-2-yl)methylene)malononitrile (**2a**)

Red solid (yield 19%). $R_f = 0.31$ (Hex:EtOAc = 3:1). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.74 (s, 1H), 7.67 (d, 1H, $J = 4.2$ Hz), 7.53 (d, 2H, $J = 8.7$ Hz), 7.35-7.29 (m, 5H), 7.16-7.13 (m, 6H), 7.05 (d, 2H, $J = 8.7$ Hz). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 157.4, 150.6, 150.1, 146.8, 140.7, 133.3, 129.8, 127.8, 125.7, 125.0, 124.6, 123.5, 121.9, 114.8, 114.0, 75.2. MALDI-MS: m/z calcd for $C_{26}H_{17}N_3S^+$ 403.1143, found 403.0908. Anal. (%): calcd (found) for $C_{26}H_{17}N_3S$: C 77.39 (76.79), H 4.25 (4.07), N 10.41 (10.14).

2.4.5. 2-((5-(4-(Dip-tolylamino)phenyl)thiophen-2-yl)methylene)malononitrile (**2b**)

Red solid (yield 20%). $R_f = 0.35$ (Hex:EtOAc = 5:1). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.73 (s, 1H), 7.66 (d, 1H, $J = 4.2$ Hz), 7.49 (d, 2H, $J = 9.0$ Hz), 7.30 (d, 1H, $J = 4.2$ Hz), 7.12 (d, 4H, $J = 8.2$ Hz), 7.04 (d, 4H, $J = 8.5$ Hz), 6.97 (d, 2H, $J = 8.9$ Hz) 2.34 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 191.3, 157.8, 150.5, 144.2, 140.7, 134.4, 133.0, 130.4, 127.7, 125.9, 124.1, 123.2, 120.7, 114.9, 114.0, 74.8, 21.1. MALDI-MS: m/z calcd for $C_{28}H_{21}N_3S^+$ 431.1456, found 431.1379. Anal. (%): calcd (found) for $C_{28}H_{21}N_3S$: C 77.93 (77.09), H 4.90 (4.54), N 9.74 (9.67).

2.4.6. 2-((5-(4-(Bis(4-methoxyphenyl)amino)phenyl)thiophen-2-yl)methylene)malononitrile (**2c**)

Black solid (yield 22%). $R_f = 0.24$ (Hex:EtOAc = 3:1). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.71 (s, 1H), 7.64 (d, 1H, $J = 4.2$ Hz), 7.42 (d, 2H, $J = 8.8$ Hz), 7.28 (d, 1H, $J = 4.2$ Hz), 7.10 (d, 4H, $J = 8.9$ Hz), 6.87 (d, 6H, $J = 8.9$ Hz), 3.82 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 158.0, 157.0, 151.0, 150.4, 140.9, 139.6, 132.8, 127.8, 127.7, 123.3, 123.0, 119.0, 115.2, 115.0, 114.1, 74.4, 55.7. MALDI-MS: m/z calcd for $C_{28}H_{21}N_3O_2S^+$ 463.1345, found 463.1473. Anal. (%): calcd (found) for $C_{28}H_{21}N_3O_2S$: C 72.55 (71.71), H 4.57 (4.33), N 9.06 (9.11).

2.4.7. 2-((5-(4-(Diphenylamino)phenyl)furan-2-yl)methylene)malononitrile (**3a**)

Red solid (yield 60%). $R_f = 0.10$ (Hex:EtOAc = 5:1). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.69 (d, 2H, $J = 9.0$ Hz), 7.34-7.29 (m, 5H), 7.24-7.05 (m, 10H), 6.81 (d, 1H, $J = 3.9$ Hz). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 189.8, 150.4, 147.0, 146.7, 140.6, 129.8, 127.2, 125.9, 124.7, 121.5, 120.7, 115.2, 114.2, 108.6, 73.3. MALDI-MS: m/z calcd for