JOC Article
pubs.acs.org/joc

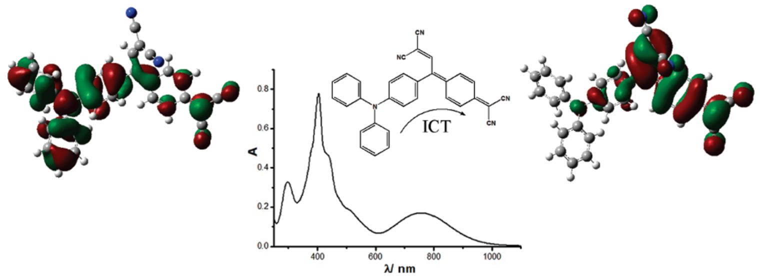
Synthesis, Crystal Structures, and Photophysical Properties of Triphenylamine-Based Multicyano Derivatives

Xianglin Tang,[†] Weimin Liu,[†] Jiasheng Wu,[†] Chun-Sing Lee,*[,‡] Juanjuan You,[†] and Pengfei Wang*[,†]

[†] *Key Laboratory of Photochemical Conversion and Optoelectronic Materials, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing, 100190, China, and* [‡] *Center of Super-Diamond and Advanced Films (COSDAF), Department of Physics and Materials Science, City University of Hong Kong, Hong Kong SAR, China*

apcslee@cityu.edu.hk; wangpf@mail.ipc.ac.cn

Received July 30, 2010



A new series of intramolecular charge transfer (ICT) molecules were synthesized by attaching various strong electron-withdrawing groups to a triphenylamine backbone. Relationships between chemical structures and optoelectronic properties of these compounds were investigated with X-ray diffraction, cyclic voltammetry, absorption spectroscopy, and density functional theory calculations. It is shown that the compounds exhibit intensive ICT interactions leading to substantial extension of their absorption spectral response, which may be potentially used for efficient solar cells.

Introduction

Electron-rich triphenylamine-based derivatives have been widely investigated and applied in organic field-effect transistors,[1] organic light-emitting diodes (OLED),[2] as well as second-order nonlinear optical devices.[3] In the past few years, organic solar cells based on triphenylamine derivatives have been developed.[4] On the other hand, dye-sensitized solar cells based on metal-free organic dyes have attracted considerable attention for their high absorption coefficients, tunable functional groups, and simple synthetic procedures.[5]

One possible solution for extending the absorption spectral response of organic dyes consisting of electron accepting and donating parts is to increase the conjugation length bridging these parts. However, intermolecular aggregation of dyes with long chain length can reduce their energy conversion efficiency.[6] Another option is to introduce stronger electron-withdrawing groups to get a D-π-A structure within the molecule.[7] With this approach, absorption spectra of

---

(1) Song, Y.; Di, C.; Yang, X.; Li, S.; Xu, W.; Liu, Y.; Yang, L.; Shuai, Z.; Zhang, D.; Zhu, D. *J. Am. Chem. Soc.* **2006**, *128*, 15940.

(2) (a) Kuwabara, Y.; Ogawa, H.; Inada, H.; Noma, N.; Shirota, Y. *Adv. Mater.* **1994**, *6*, 677. (b) Tao, Y. T.; Wang, Q.; Ao, L.; Zhong, C.; Yang, C. L.; Qin, J. G.; Ma, D. G. *J. Phys. Chem. C* **2010**, *114* (1), 601.

(3) (a) Lambert, C.; Gaschler, W.; Schmälzlin, E.; Meerholz, K.; Bräuchle, C. *J. Chem. Soc., Perkin Trans. 2* **1999**, 577. (b) Faccini, M.; Balakrishnan, M.; Diemeer, M. B. J.; Hu, Z.-P.; Clays, K.; Asselberghs, I.; Leinse, A.; Driessen, A.; Reinhoudt, D. N.; Verboom, W. *J. Mater. Chem.* **2008**, *18*, 2141.

(4) (a) Cravino, A.; Leriche, P.; Alévêque, O.; Roquet, S.; Roncali, J. *Adv. Mater.* **2006**, *18*, 3033. (b) He, C.; He, Q.; Yi, Y.; Wu, G.; Bai, F.; Shuai, Z.; Li, Y. *J. Mater. Chem.* **2008**, *18*, 4085. (c) Wu, G.; Zhao, G.; He, C.; Zhang, J.; He, Q.; Chen, X.; Li, Y. *Sol. Energy Mater. Sol. Cells* **2009**, 108. (d) Zhao, G.; Wu, G.; He, C.; Bai, F.-Q.; Xi, H.; Zhang, H.-X.; Li, Y. *J. Phys. Chem. C* **2009**, *113* (6), 2636.

(5) (a) Horiuchi, T.; Miura, H.; Sumioka, K.; Uchida, S. *J. Am. Chem. Soc.* **2004**, *126*, 12218. (b) Ferrere, S.; Zaban, A.; Gregg, B. A. *J. Phys. Chem. B* **1997**, *101*, 4490. (c) Ito, S.; Zakeeruddin, S. M.; Humphry-Baker, R.; Liska, P.; Charvet, R.; Comte, P.; Nazeeruddin, M. K.; Péchy, P.; Takata, M.; Miura, H.; Uchida, S.; Grätzel, M. *Adv. Mater.* **2006**, *18*, 1202. (d) Ito, S.; Miura, H.; Uchida, S.; Takata, M.; Sumioka, K.; Liska, P.; Comte, P.; Péchy, P.; Grätzel, M. *Chem. Commun.* **2008**, 5194.

(6) (a) Qin, P.; Yang, X.; Chen, R.; Sun, L. C.; Marinado, T.; Edvinsson, T.; Boschloo, G.; Hagfeldt, A. *J. Phys. Chem. C* **2007**, *111*, 1853. (b) Hagberg, D. P.; Marinado, T.; Karlsson, K. M.; Nonomura, K.; Qin, P.; Boschloo, G.; Brinck, T.; Hagfeldt, A.; Sun, L. *J. Org. Chem.* **2007**, *72*, 9550.

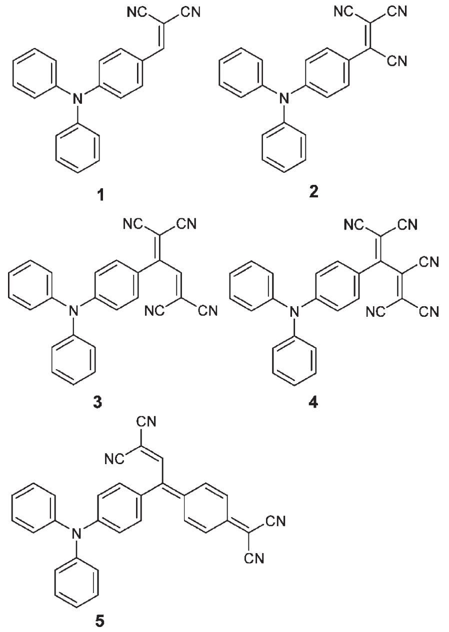
(7) (a) Roquet, S.; Cravino, A.; Leriche, P.; Alévêque, O.; Frère, P.; Roncali, J. *J. Am. Chem. Soc.* **2006**, *128*, 3459. (b) Leriche, P.; Frère, P.; Cravino, A.; Alévêque, O.; Roncali, J. *J. Org. Chem.* **2007**, *72*, 8332.

DOI: 10.1021/jo101456v

these compounds can be easily tuned via controlling the extent of intramolecular charge transfer (ICT).

Common acceptors in these dyes are mostly weak electron-withdrawing groups such as cyanoacrylic acid and rhodanine-3-acetic acid.[8] It is well-known that the cyano group is one of the strongest electron-withdrawing groups. Stronger electron-accepting effects can be further obtained by introducing several cyano groups into a conjugated system. For example, tetracyanoethene (TCNE) and 7,7,8,8-tetracyanoquinodimethane (TCNQ) as stable strong electron acceptors are widely used in many fields.[9] In this context, we designed and synthesized a new series of ICT compounds by incorporating the triphenylamine moiety (electron donor) with different multicyano groups (electron acceptor) (**3**−**5**, Chart 1). To explore the relationship between chemical structures and properties of these compounds, we also synthesized other compounds (**1** and **2**, Chart 1) for comparison. Properties of all these triphenylamine-based derivatives (**1**−**5**) were investigated with X-ray diffraction, cyclic voltammetry, absorption spectroscopy, and density functional theory calculations.

CHART 1. Structures of Compounds 1−5



Results and Discussion

Synthesis. Aldehyde **6** was synthesized according to a previously reported method.[10] Dicyanovinyl derivative **1** was synthesized by condensation of **6** with malonodinitrile.[11] The reaction was carried out in ethanol at room temperature with triethylamine as catalyst and produced **1** in 80% yield (Scheme 1). **2** was synthesized straightforwardly in high yield by reacting triphenylamine with an excess of tetracyanoethylene (TCNE) in DMF.[3]

Compounds **3**−**5** were obtained from the same intermediate **8**. According to a reported route,[12] compound **8** has to be synthesized by using palladium chemistry with diphenylamine as starting material in four steps. Here the procedure was simplified and compound **8** can be obtained in excellent yield via three simple steps without any palladium catalyst from triphenylamine. First, triphenylamine underwent formylation to form **6**. Then, a Wittig reaction of **6** with CBr_4 and PPh_3 led to dibromoalkene **7** at room temperature in 1 h. Finally, treatment of **7** with *n*-BuLi generated a bromoalkyne intermediate, which via dehydrohalogenation gave the alkyne **8** upon aqueous workup. [2 + 2] cycloaddition[13] of alkyne **8** with TCNE and 7,7,8,8-tetracyanoquinodimethane (TCNQ) yielded the terminal compounds **3** and **5**, respectively (Table 1). In both cases, the reaction proceeded at room temperature in dichloromethane for 5 h and provided the products with nearly unity yields. Cyanoalkyne **9** was obtained in 85% yields by treatment of alkyne **8** with successively *n*-BuLi and PhOCN at low temperature. Addition of the electron-withdrawing group lowered the reactivity of compound **9**. The corresponding reaction of **9** with TCNE required much longer time than alkyne **8**, and gave compound **4** with 60% yield. All new compounds were isolated as deep colored solids and found to be stable under ambient conditions. Identities and structures of the compounds were confirmed with NMR and mass spectrometry.

X-ray Structures. Single crystals of **3**, **4**, and **5** suitable for X-ray crystallographic analysis were obtained by slow diffusion of hexane into CH_2Cl_2 solution of the compounds at ambient temperature. Common features in compounds **3** to **5** were observed. First, the N atom in the triphenylamine group has an sp^2 geometry.[14] The three central C−N single bonds are nearly coplanar with the benzene ring bearing the acceptors, while the other two benzene rings are twisted. On the other hand, due to strong repulsion arising from the steric

SCHEME 1. Synthesis of Compounds 1−5

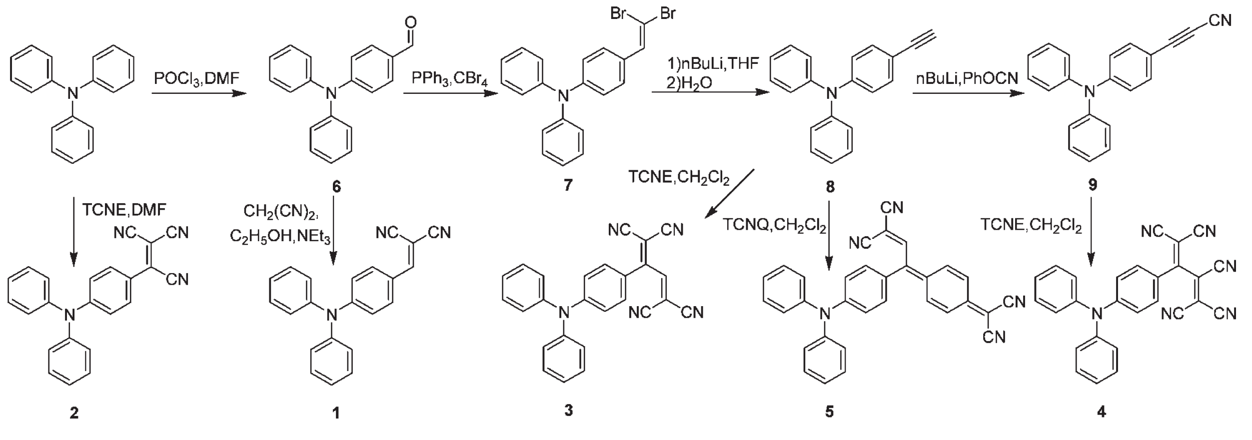


TABLE 1. Crystallographic Data of 3−5 and Theoretical Calculation Data for 1−5

	δr [Å]	θ_{exp}[a] [deg]	θ_{cal}[b] [deg]	δ_{H}[c] [ppm]
1			0.5	7.72
2			15.5	7.95
3	0.034	32.1	44.1	7.33
4	0.046	26.3	26.8	7.53
5	0.032	50.9	56.0	7.10

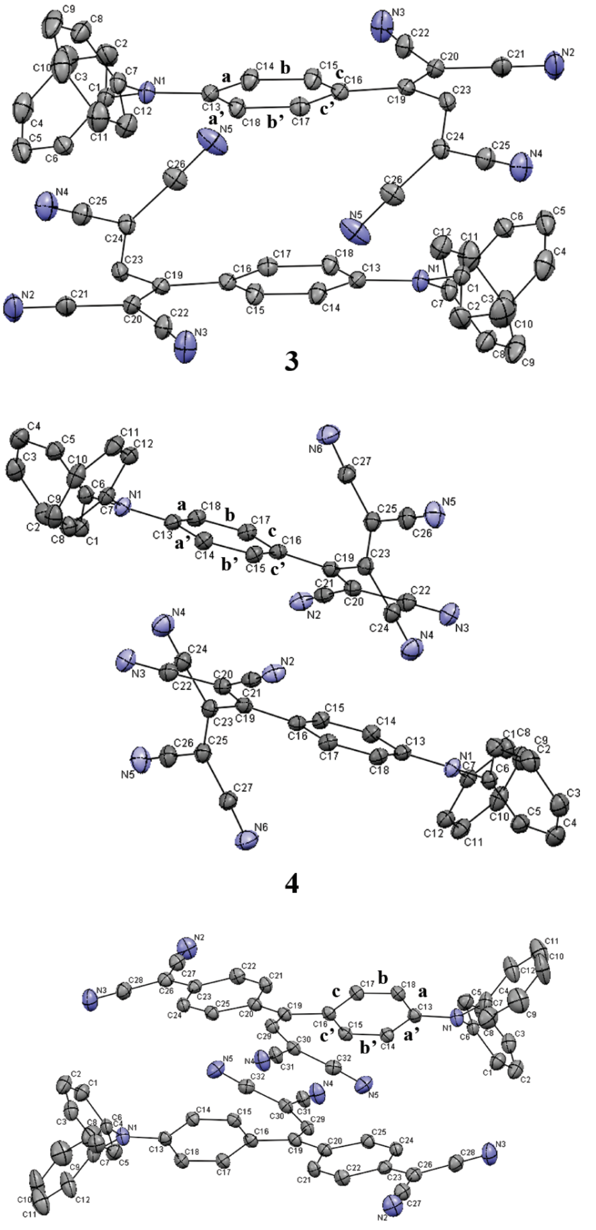
[a] The torsion angle between cyanovinyl moiety and donor rings determined from crystal structure. [b] The torsion angle determined from theoretical calculation. [c] ^{1}H NMR chemical shifts of the protons in the ortho position to the acceptor (400 MHz) in $CDCl_3$.

hindrance of cyano groups, intense distortions were observed in all the acceptor moieties. In particular, rotation of the two vinyl groups around the central single bond disturbs the planarity of the butadiene. For example, torsion angles of respectively 41°, 54°, and 22° in the single bonds were observed in **3**−**5**. However, the torsion angle between the vinyl moieties and the benzene rings changes with an opposite trend. The measured θ values for **3**(C(20)−C(19)−C(16)−C(17)), **4**(C(20)−C(19)−C(16)−C(17)), and **5**(C(20)−C(19)−C(16)−C(17)) (for atom labels, see Figure 1) are respectively 32°, 26°, and 51°. The more planar structure indicates more conjugation between the vinyl groups and the donor moieties.

Charge transfer from the donor to the acceptor parts is accompanied by bond length alternation in the bridging benzene ring. The amount of bond length variation reflects the extent of CT in the ground state, and can be expressed by the quinoid character (δr)[15] (eq 1, see Figure 1 for the definition of bonds a, a', b, b', c, and c').

$$\delta r = ([(a+a')/2-(b+b')/2]+[(c+c')/2-(b+b')/2])/2 \tag{1}$$

The δr value is 0 for a single benzene molecule. Upon introduction of donor and/or acceptor moieties, bond length variations in the ring would lead to changes in the δr value. The δr value in fully quinoid rings varies between 0.08 and 0.10. For the bridging benzene ring in **5**, the δr value obtained from the X-ray data is 0.032. In **3** and **4**, higher values of 0.034 and 0.046 were observed, respectively, due to increased coplanarity between the vinyl groups and the attached benzene rings. These values indicate efficient ICT interaction in the ground state.



3

4

5

FIGURE 1. Molecular structures of **3**, **4**, and **5** with ellipsoids shown at the 30% probability level (hydrogen atoms are omitted for clarity).

Changes in electron distribution resulting from the CT would also influence the chemical shifts of the protons in the bridging benzene ring. Downfield shifts of the protons in the ortho position to the acceptor moiety increase from 7.10 for **5** to 7.33 and 7.53 respectively for **3** and **4**. The trend in chemical shifts of the protons is consistent with that of the δr values. The chemical shifts of the nearby protons may indicate the efficiency of ground-state ICT interaction.[16] Taking

---

(8) (a) Marinado, T.; Hagberg, D. P.; Hedlund, M.; Edvinsson, T.; Johansson, E. M. J.; Boschloo, G.; Rensmo, H.; Brinck, T.; Sun, L.; Hagfeldt, A. *Phys. Chem. Chem. Phys.* **2009**, *11*, 133. (b) Wiberg, J.; Marinado, T.; Hagberg, D. P.; Sun, L.; Hagfeldt, A.; Albinsson, B. *J. Phys. Chem. C* **2009**, *113*, 3881.

(9) (a) Ferraris, J.; Cowan, D. O.; Walatka, V., Jr.; Perlstein, J. H. *J. Am. Chem. Soc.* **1973**, *95*, 948. (b) Webster, O. W.; Mahler, W.; Benson, R. E. *J. Org. Chem.* **1960**, *25*, 1470. (c) Vellaichamy, G.; Sergiy, V. R.; Jay, K. K. *J. Am. Chem. Soc.* **2003**, *125*, 2559.

(10) Lai, G.; Bu, X. R.; Santos, J.; Mintz, E. A. *Synlett* **1997**, 1275.

(11) Chen, X.-H.; Zhao, Z.; Liu, Y.; Lu, P.; Wang, Y.-G. *Chem. Lett.* **2008**, *37*, 570.

(12) McIlroy, S. P.; Cló, E.; Nikolajsen, L.; Frederiksen, P. K.; Nielsen, C. B.; Mikkelsen, K. V.; Gothelf, K. V.; Ogilby, P. R. *J. Org. Chem.* **2005**, *70*, 1134.

(13) (a) Cairns, T. L.; Carboni, R. A.; Caffman, D. D.; Engelhardt, V. A.; Heckert, R. E.; Little, E. L.; McGeer, E. G.; McKusick, B. C.; Middleton, W. J. *J. Am. Chem. Soc.* **1957**, *79*, 2340. (b) Kivala, M.; Boudon, C.; Gisselbrecht, J.-P.; Seiler, P.; Gross, M.; Diederich, F. *Chem. Commun.* **2007**, 4731.

(14) Palsson, L.-O.; Wang, C.; Batsanov, A. S.; King, S. M.; Beeby, A.; Monkman, A. P.; Bryce, M. R. *Chem.—Eur. J.* **2010**, *16*, 1470.

(15) (a) Dehu, C.; Meyers, F.; Brédas, J. L. *J. Am. Chem. Soc.* **1993**, *115*, 6198. (b) Hilger, A.; Gisselbrecht, J.-P.; Tykwinski, R. R.; Boudon, C.; Schreiber, M.; Martin, R. E.; Lüthi, H. P.; Gross, M.; Diederich, F. *J. Am. Chem. Soc.* **1997**, *119*, 2069.

(16) Michinobu, T.; Boudon, C.; Gisselbrecht, J.-P.; Seiler, P.; Frank, B.; Moonen, N. N. P.; Gross, M.; Diederich, F. *Chem.—Eur. J.* **2006**, *12*, 1889.

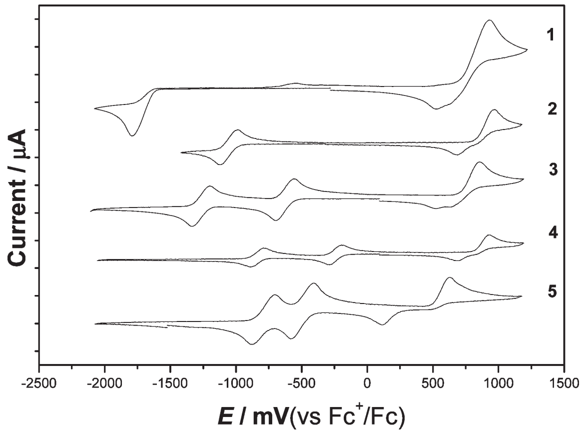


FIGURE 2. Cyclic voltammograms of compounds **1**−**5** in CH_2Cl_2. All solutions contained tetrabutylammonium hexafluorophosphate ($TBAPF_6$, 0.1 M) as the supporting electrolyte, scan rate is 100 mV s^{-1}, using glassy carbon as the working electrode, Pt wire as the counter electrode, and $Ag/AgNO_3/DMF$ as the reference electrode.

TABLE 2. Cyclic Voltammetric Data (in 0.10 M Bu_4NPF_6/CH_2Cl_2, vs Fc^+/Fc, Scan rate 100 mV/s) and Optical Gap Determined from the Optical Absorption Edge (in CH_2Cl_2) for Compounds 1−5

	E_{ox} [V]	E_{red} [V]	ΔE_{op}[c] [eV]	ΔE_{el}[d] [V]
1	0.95	−1.79[a]	2.47	2.74
2	0.97	−1.05	1.84	2.02
3	0.85	−0.62 −1.27[b]	1.44	1.47
4	0.93	−0.24 −0.84[b]	1.31	1.17
5	0.64	−0.49 −0.79[b]	1.09	1.13

[a] Irreversible process. [b] Second reduction potentials. [c] Optical gap estimated from the absorption edge. [d] Electrochemical gap $\Delta E_{el} = E_{ox,1} - E_{red,1}$.

account of the X-ray and NMR data, the extent of ICT increases in the order of **5** < **3** < **4**.

Electrochemical Experiments. As shown in Figure 2, cyclic voltammograms of compounds **1**−**5** have been measured in CH_2Cl_2 with 0.1 M tetrabutylammonium hexafluorophosphate as the supporting electrolyte. Compound **1** undergoes an irreversible reduction, whereas compound **2** shows one reversible reductive step. Two reversible reduction processes were observed in **3** to **5** indicating formation of stable anions and dianions. As expected, increasing the number of cyano groups in the acceptor moieties leads to enhancement of the acceptor strength and thus anodic shift of the first reduction potential. For example, the first reduction potential shifts toward more positive values from −1.79 V for **1** to −1.05, −0.62, −0.49 V respectively for **2**, **3**, and **5** (Table 2). The value of **4** is even comparable to that of TCNQ (−0.25 vs −0.24 V). However, the second reduction in **5** (−0.79 V) is easier than that in **3** (−1.27 V) and **4** (−0.84 V), which can be explained by the more conjugative acceptor moiety in **5**. As for oxidation, the diphenylamino groups in all compounds show quasi-reversible processes due to the unprotected para-position of the phenyl groups.[3a,17] Electron density transfer from donor to acceptor hinders the oxidation of donor, and thereby the potential of the anodic peak reflects the efficiency of ground state ICT directly. The oxidation potentials of **3** and **4** shift to 0.85 and 0.93 V, respectively, relative to that of **5** (0.64 V). Furthermore, the oxidation processes occur at slightly more positive potentials for **1** (0.95 V) and **2** (0.97 V). The anodic shift resulting from efficient intramolecular CT is presumably a consequence of the trade-off between acceptor strength and the coplanarity between the donor and the acceptor moieties.

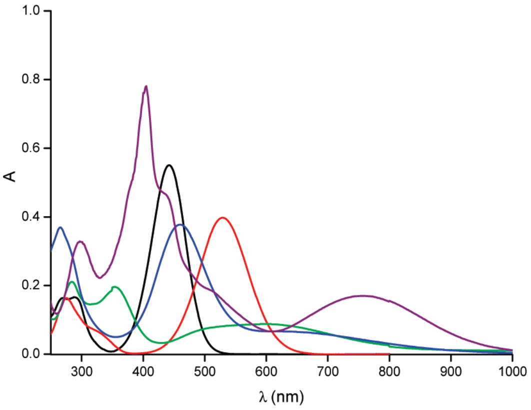


FIGURE 3. Absorption spectra of compounds **1** (black), **2** (red), **3** (green), **4** (blue), and **5** (purple) in CH_2Cl_2 at 298 K.

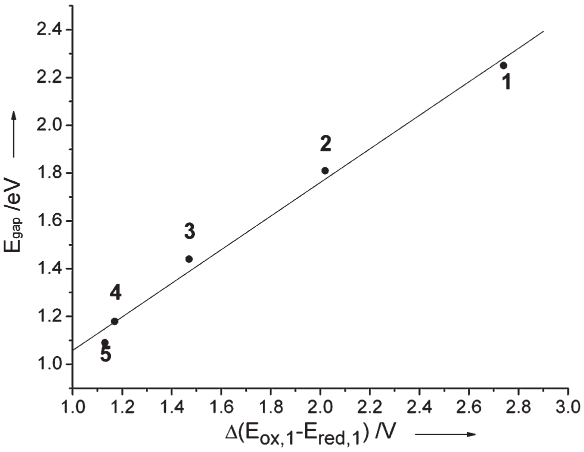


FIGURE 4. Linear correlation between the optical gap E_{gap} and the electrochemical gap $\Delta(E_{ox,1} - E_{red,1})$ for compounds **1**−**5**.

UV−Vis Spectroscopy. Absorption spectra of all compounds recorded in CH_2Cl_2 show their first absorption band in the 270−330 nm region and subsequent bands of lower energy. On the basis of the spectrum of triphenylamine, the first absorption band can be attributed to a $\pi-\pi^*$ transition. The other bands can be assigned to ICT transitions between triphenylamine and different acceptors. The origin of the ICT bands is further confirmed by the solvatochromic effects as shown in the Supporting Information.[18] While the spectra of **1** and **2** show only one intense ICT band with their maximum shifting from 440 to 530 nm, an additional weak and broad ICT band at longer wavelengths can be observed in **3**, **4**, and **5** due to the additional cyanovinyl group (Figure 3). In addition, the TCNQ moiety in **5** may result in a more complex absorption band, which is obviously different

---

[17] Tsai, M.-H.; Lin, H.-W.; Su, H.-C.; Ke, T.-H.; Wu, C.-c.; Fang, F.-C.; Liao, Y.-L.; Wong, K.-T.; Wu, C.-I. *Adv. Mater.* **2006**, *18*, 1216.

[18] Suppan, P. *J. Photochem. Photobiol. A* **1990**, *50*, 293.

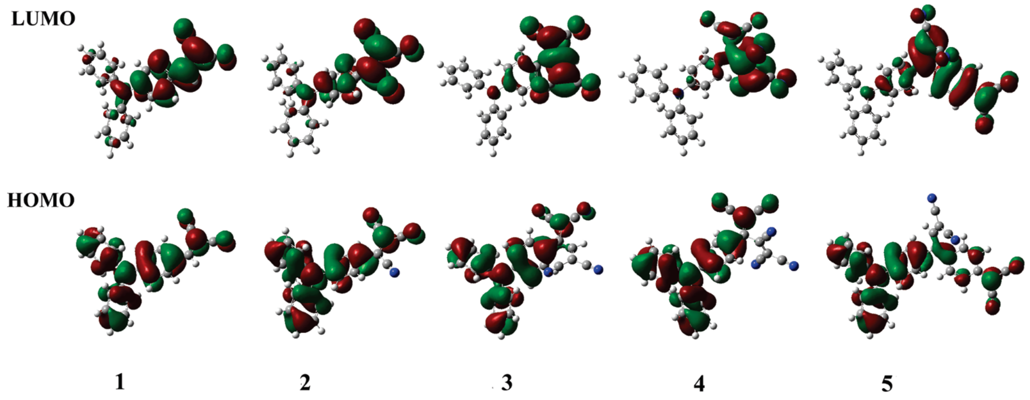


FIGURE 5. Spatial distributions of the calculated HOMOs and LUMOs of **1**−**5**.

from that of compound **1**−**4**. It is found that there exists a shoulder peak centered at 400 nm in compound **5**, which can be ascribed to the characteristic peak of TCNQ.[19] Furthermore, the optical gaps estimated from the absorption edge of the UV−vis spectra show a linear correlation ($R = 0.995$) with the electrochemical gaps $\Delta(E_{\mathrm{ox},1} - E_{\mathrm{red},1})$, indicating that the same orbitals are involved in both optical and electrochemical band gaps for **1**−**5** (Figure 4).[20] Although the X-ray crystal structures and electrochemical results indicate that **5** has the lowest extent of ICT interaction in the ground state, the absorption maximum (750 nm) for **5** is the longest in the whole series. This is in agreement with recent studies that bathochromic shift of the ICT band in the UV−vis spectrum is generally not a good indicator for the extent of ICT interaction.[21] Interestingly, as shown in Figure 3, the UV−vis spectra of **3**, **4**, and **5** feature very broad absorption bands, and the broadest absorption bands of **5** may result from the longest conjugated system. This suggests that these ICT molecules can absorb photons over a wide spectral range.

Theoretical Basis. To investigate the geometric and electronic properties of compounds **1**−**5**, quantum calculations using the Gaussian 03 program have been performed.[22] The calculations were optimized by using the restricted B3LYP/6-31G(D,P) functions at a density functional theory (DFT) level. The calculated dihedral angles between the planes of acceptor moieties and the conjugated benzene rings are listed in Table 1. As expected, the results of geometry optimizations show good correlations with the experimental data obtained from single crystal structures for **3**, **4**, and **5**. For **4**, the calculated angle (26.8°) is in good agreement with the experimental value (26.3°). On the other hand, the calculated angles in **3** and **5** are slightly larger than the corresponding experimental values. In contrast, DFT calculations indicated smaller dihedral angles in **1** and **2** when compared to that in **4**, which suggest that **1** and **2** should have more planar conformations. The small discrepancy between the experimental and the theoretical results may be caused by the absence of intermolecular interactions in the latter. The calculated HOMOs and LUMOs of **1**−**5** are illustrated in Figure 5. The density in the HOMOs of all the compounds is mainly concentrated on the electron-donating triphenylamine moiety with low coefficients on the electron-withdrawing cyanovinyl group. The distributions of HOMOs in all compounds directly show the ICT interactions. The LUMOs are mainly located on the electron-withdrawing groups. The separation between HOMO and LUMO indicates that substantial charge transfer from the donor moiety to the acceptor moiety when molecules are excited.

Conclusions

A new series of triphenylamine-based multicyano derivatives have been synthesized in high yields. The electronic properties and the efficiency of the ICT interactions were considered from their crystallography, NMR chemical shifts of hydrogen atoms, and electrochemical data. The electrochemical analysis of the effect of the number of cyano groups shows that increasing the number of cyano groups leads to an increase of the acceptor strength. Through analysis of the physicochemical properties of the new chromophores, it was observed that the extent of intramolecular charge transfer can be enhanced by using a stronger acceptor and/or a more planar structure between the cyanovinyl moiety and the donor ring. Both the X-ray crystallographic analysis and theoretical calculations reveal that the acceptors in these new chromophores **3**−**5** are highly distorted. Comparing with **1** and **2**, additional strong intramolecular charge transfer bands in the near-infrared region were observed in **3**−**5**. As a result, **3**−**5** have board absorption spectra responses over the solar spectrum. These results suggest that the present approach of molecular engineering might pave a potential route for developing materials suitable for applications in solar energy conversion.

---

(19) Ong, W.; McCarley, R. L. *Org. Lett.* **2005**, *7*, 1287.

(20) Kivala, M.; Boudon, C.; Gisselbrecht, J.-P.; Enko, B.; Seiler, P.; Müller, I. B.; Langer, N.; Jarowski, P. D.; Gescheidt, G.; Diederich, F. *Chem.—Eur. J.* **2009**, *15*, 4111.

(21) (a) Kivala, M.; Diederich, F. *Acc. Chem. Res.* **2009**, *42*, 235. (b) Spitler, E. L.; Monson, J. M.; Haley, M. M. *J. Org. Chem.* **2008**, *73*, 2211.

(22) 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 E.01; Gaussian, Inc., Wallingford, CT, 2004.

Experimental Section

Synthesis of 4-(2,2-Dibromovinyl)-*N*,*N*-diphenylbenzenamine (7). 4-(Diphenylamino)benzaldehyde **6** (1.36 g, 5.0 mmol) was added to a solution of CBr_4 (3.31 g, 10.0 mmol) and PPh_3 (5.25 g, 20.0 mmol) in anhydrous dichloromethane (50 mL). After the solution was stirred for 60 min at room temperature, the reaction was quenched with water (50 mL) and extracted with dichloromethane (3 × 50 mL). The combined organic layers were washed with water and brine, then dried over Mg_2SO_4. After the solvent was removed under a reduced pressure, the crude residue was purified by column chromatography on SiO_2 with ethyl acetate−petroleum ether (1:1) to afford the desired product **7** (1.5 g, 71%) as light yellow solid. Mp 122−123 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.99 (d, 2H, J = 8.7 Hz), 7.06 (m, 6H), 7.27 (m, 4H), 7.38 (s, 1H), 7.43 (d, 2H, J = 8.7 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 87.1, 122.0, 123.8, 125.2, 128.5, 129.6, 136.4, 147.3, 148.3; HR-EI-MS *m*/*z* calcd for $C_{20}H_{15}N^{79}Br^{81}Br^+$ 428.9551, found 428.9545.

Synthesis of (4-Ethynylphenyl)diphenylamine (8). *n*-BuLi (27.50 mmol, 10 mL of a 2.75 M solution in hexane) was added dropwise to a stirred solution of **7** (2.0 g, 4.7 mmol) in anhydrous THF (30.0 mL) under a nitrogen atmosphere at −78 °C. The solution was stirred at −78 °C for 1 h then warmed to room temperature. The reaction mixture was quenched with brine and extracted with ethyl acetate. The combined organic layers were washed with water and brine, then dried over Mg_2SO_4. The solvent was removed under a reduced pressure. Purification by column chromatography on SiO_2 eluting with ethyl acetate−petroleum ether (1:99) afforded the desired product **8** (1.2 g, 95%) as a light yellow solid. Mp 108−109 °C; spectroscopic data were consistent with those reported previously[23] for this compound; EI-MS *m*/*z* $C_{20}H_{15}N^+$ 269.

Synthesis of 3-(4-(Diphenylamino)phenyl)propiolonitrile (9). To a solution of compound **8** (800 mg, 2.9 mmol) dissolved at −78 °C under nitrogen atmosphere in anhydrous THF (15.0 mL) was added *n*-BuLi (13.8 mmol, 5.0 mL of a 2.75 M solution in hexane) dropwise. After 10 min of stirring at −78 °C, PhOCN (1.3 g, 11 mmol) in THF (5.0 mL) was added slowly. The solution was stirred for 30 min at −78 °C and warmed to room temperature. The reaction mixture was quenched with brine and extracted with ethyl acetate. The organic solution was washed with water and brine, then dried over Mg_2SO_4. After removal of the solvent under a reduced pressure, the residue was chromatographed on SiO_2 (eluent 1:50 ethyl acetate/petroleum ether) to give **9** (800 mg, 90%) as a yellow solid. Mp 139−140 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.92 (d, 2H, J = 8.8 Hz), 7.15 (m, 6H), 7.33 (m, 4H), 7.38 (d, 2H, J = 8.8 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 62.8, 84.6, 106.3, 107.9, 119.9, 125.2, 126.2, 129.9, 134.8, 146.1, 151.1; EI-HR-MS *m*/*z* calcd for $C_{21}H_{14}N_2^+$ 294.1157, found 294.1160.

Synthesis of Compounds 3 and 5. To a solution of compound **8** (200 mg, 0.74 mmol) in CH_2Cl_2 (10 mL) was added TCNE (100 mg, 0.78 mmol) or TCNQ (150 mg, 0.74 mmol). The mixture was stirred for 5 h at room temperature. After evaporation of the solvent in vacuo, the solid was dissolved in a minimal amount of CH_2Cl_2, then *n*-hexane was added until precipitation started. Crystallization at 0 °C afforded the desired pure products. Compound **3** was isolated pure in 90% yield as dark blue glassy solid. In the case of **5**, pure product was obtained in 88% yield as dark green glassy solid.

2-(4-(Diphenylamino)phenyl)buta-1,3-diene-1,1,4,4-tetracarbonitrile (3). Mp 184−185 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.01 (d, 2H, J = 9 Hz), 7.19 (m, 6H), 7.33 (d, 2H, J = 9 Hz), 7.36 (m, 4H), 8.01 (s,1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 83.7, 97.9, 108.0, 109.0, 111.7, 112.3, 112.9, 119.3, 121.5, 126.3, 126.8, 130.1, 131.6, 145.2, 153.8, 155.1, 160.1; EI-HR-MS *m*/*z* calcd for $C_{26}H_{15}N_5^+$ 397.1327, found 397.1330.

2-(4-(3,3-Dicyano-1-(4-(diphenylamino)phenyl)allylidene)cyclohexa-2,5-dienylidene)malononitrile (5). Mp 258−260 °C; ^{1}HNMR (400 MHz, $CDCl_3$) δ 7.06 (d, 2H, J = 8.8 Hz), 7.10 (d, 2H, J = 8.8 Hz), 7.17 (m, 6H), 7.33 (m, 6H), 7.56 (s, 2H), 8.17 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 79.8, 89.9, 92.2, 110.5, 111.7, 113.6, 114.1, 121.2, 125.2, 126.2, 127.4, 129.9, 131.4, 133.1, 137.5, 146.1, 146.3, 150.9, 151.7, 152.9, 154.5; EI-HR-MS *m*/*z* calcd for $C_{32}H_{19}N_5^+$ 473.1640, found 473.1643.

Synthesis of 3-(4-(Diphenylamino)phenyl)buta-1,3-diene-1,1,2,4,4-pentacarbonitrile (4). To a solution of compound **9** (800 mg, 2.72 mmol) in CH_2Cl_2 (40 mL) was added TCNE (350 mg, 2.73 mmol). The mixture was stirred for 48 h at room temperature. After evaporation of the solvent in vacuo, the residue was chromatographed on SiO_2 (eluent 1:4 petroleum/CH_2Cl_2) to give a green product. The solid was dissolved in a minimal amount of CH_2Cl_2, then *n*-hexane was added until precipitation started. Crystallization at 0 °C afforded **4** (650 mg, 56%) as a green solid. Mp 208−209 °C; ^{1}HNMR (400 MHz, $CDCl_3$) δ 6.96 (d, 2H, J = 9.2 Hz), 7.23 (d, 4H, J = 7.4 Hz), 7.31 (m, 2H), 7.43 (t, 4H, J = 7.4 Hz), 7.53 (d, 2H, J = 9.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 79.1, 105.3, 108.2, 108.9, 111.1, 112.3, 112.7, 118.4, 119.2, 127.1, 127.4, 130.4, 132.0, 138.6, 144.1, 153.8, 154.9; EI-HR-MS *m*/*z* calcd for $C_{27}H_{14}N_6^+$ 422.1280, found 422.1277.

Acknowledgment. This work is financially supported by the National Natural Science Foundation of China (Grant Nos. 60778033 and 20903110), the National High Technology Research and Development Program of China (863 Program) (Grant No. 2008AA03A327), and the National Basic Research Development Program of China (973 Program) (Grant Nos. 2006CB933000 and 2009CB623703).

Supporting Information Available: ^{1}H NMR and ^{13}C NMR spectra for the new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

---

[23] Onitsuka, K.; Ohara, N.; Takei, F.; Takahashi, S. *Dalton Trans.* **2006**, 3693.