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Dye-sensitized solar cell utilizing organic dyads containing triarylene conjugates

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ABSTRACT

A series of organic dipolar compounds containing a donor (D), a bridge (B), and an acceptor (A), forming a D–B–A type of dyads, were synthesized by convenient methods and were utilized successfully on dye-sensitized solar cells. The central bridges were made of three linearly connected arylene groups, i.e., phenylenes or thiophenylenes. The donor groups were aromatic amines, i.e., either a diphenylamine or a naphthylphenylamine group. The acceptor group was a cyanoacrylic acid, which can be anchored onto the surface of TiO_2 in a photovoltaic device. These devices performed remarkably well, with a typical quantum efficiency of 5–7%, and optimal incident photon to current conversion efficiency (IPCE) exceeding 80%. The devices made with a naphthylphenylamine donor group performed slightly better than those made with a diphenylamine donor group. Compounds containing a phenylene–thiophenylene–phenylene bridge group performed better than those with other kinds of triarylene linkages. Their photochemical behaviors were analyzed by using time-dependent density functional theory (TDDFT) models with the B3LYP functional.

1. Introduction

Organic dipolar compounds containing an electron donor (D) and an electron acceptor (A), separated by a bridge group (B), have found wide applications on the new generation of optoelectronic devices.[1] Electron transfer from D to A happens rapidly upon photo-excitation to generate a charge-separated species.[2] Subsequent charge recombination may proceed within the molecule to generate a charge-transfer (CT) emission in certain cases, or it may be guided to proceed through an external circuit such as the design in dye-sensitized solar cells (DSSCs). Because the efficiency of the solar cell competes with the internal charge recombination, the lifetime of the CT state becomes a major concern for designing the dyes. In previous reports, organic dyes using aryl amine as a donor and cyanoacrylic acid as an acceptor have exhibited promising results. For the donor group, a wide choice of aryl amines have been used such as coumarin,[3] indoline,[4] cyanine,[5] merocyanine,[6] hemicyanine,[7] porphyrin,[8] etc., while most of them exhibited satisfactory performances. It has also been noticed that the structure of the bridge group played a crucial role in these devices. The function of a bridge group is twofold, i.e., acting both as a part of the light absorbing chromophore and also as a channel for transporting charges. A good bridge group should promote the absorption of light over a wide wavelength region, yet retards the rate of internal charge recombination. Linearly connected arylenes serve both purposes quite well. The flexible dihedral angles between adjacent aryl groups are twisted to a greater extend upon excitation to the CT state, while the electronic resonance is reduced and the rate of charge recombination slows down. In this report we describe our efforts in search of the best molecular structures of DSSC dyes. Triphenylamine is selected as the D group according to its outstanding performance in past literatures.[9] For the B group, a linkage containing three aryl moieties seems to fit well with the optimal distance between the centers of D and A. A series of compounds with a general formula as shown in Figure 1 were prepared. Indeed these dyes displayed remarkable performance while fabricated into photovoltaic devices.

2. Results and discussion

The synthetic sequences are outlined in Scheme 1. All compounds can be categorized in two groups, i.e., **1P** and **1N**, each are further divided into five types according to their triarylene linkages, i.e., **PPP**, **PPS**, **PSP**, **PSS**, and **SSS**, where **P** and **S** denote phenyl and thiophene groups, respectively. The syntheses are started from diarylamine, onto which the third aromatic substituent was added through Buchwald–Hartwig coupling reactions by the aid of $Pd(OAc)_2$ to build up new C–N bonds.[10] The structure of certain products exhibited twofold symmetry, e.g., 2, 5, and 9, which can be justified by their ^1H and ^{13}C NMR spectra.

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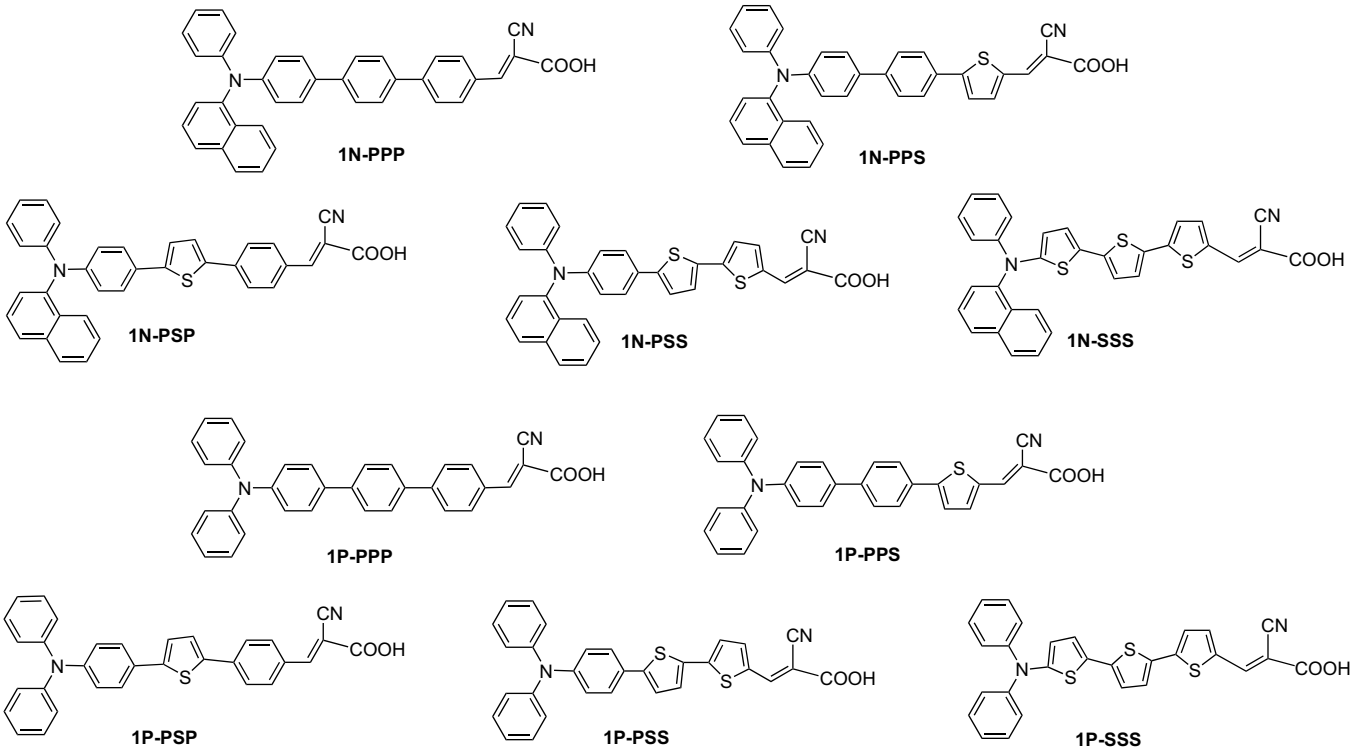


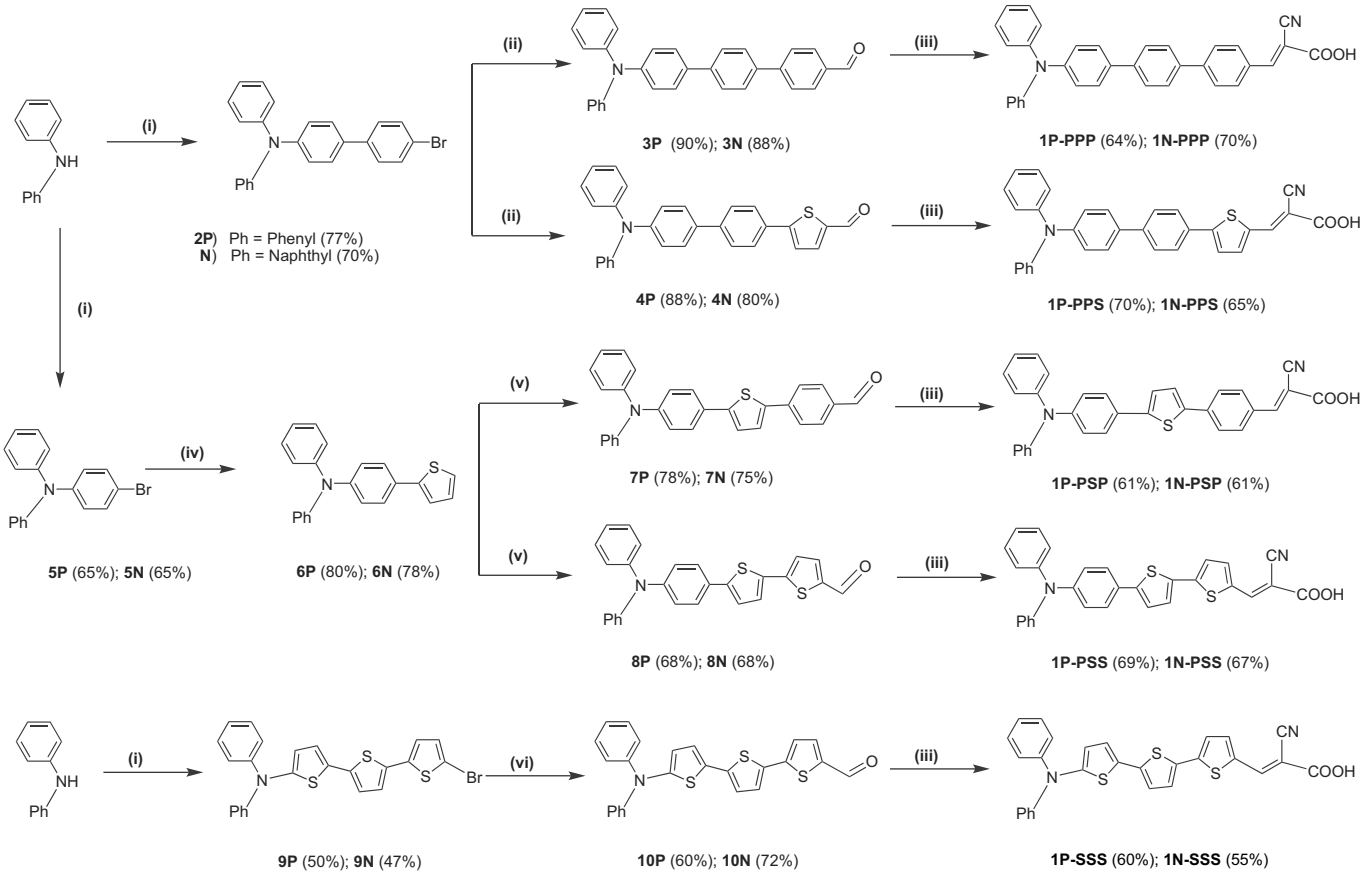
Figure 1. Organic dye structure of **1N** and **1P** series.

The trithiophenylene linkage in compounds **9P** and **9N** was completed in a single step. A subsequent formylation was done by Vilsmeier–Haack reaction to give **10P** and **10N**.[11] For compounds **2P** and **2N**, an extension of the aryl chain was achieved by Suzuki coupling reactions to yield the aldehydes **3P**, **3N**, **4P**, and **4N** in 80–90% yields.[12] The addition of a thiophene unit on **5P** and **5N** was done by Stille coupling with 2-bromothiophene to give **6P** and **6N** in ca. 80% yield.[13] A similar type of reaction was performed again to put on the third aryl groups in **7P**–**8N** in 68–78% yields. The final step was a Knoevenagel condensation with cyanoacetic acid to convert carbaldehydes to cyanoacrylic acids.[14] All final products can be crystallized into deep color solids.

The absorption spectra of organic dyes in THF solution are displayed in Figure 2. Each of these compounds exhibits a major absorption band on the long wavelength edge at λ_{max} 380–480 nm. This band exhibits a distinctive solvent shift, therefore is assigned a π–π^* transition mixed with significant CT character (Supplementary data). Upon photo-excitation, the high-lying electron, mostly localized on the triarylamine (D) moiety, migrates to cyanoacrylic acid (A) on the other side of the molecule. The electron movement is heavily coupled with the π-orbitals of the central triaryl linkage (B). The linkages containing more thiophene moieties displayed a greater bathochromic shift, e.g., **SSS**≈**PSS**>**PSP**≈**PPS**>**PPP** in both series. The high-lying π orbital in thiophene is located at a higher potential level than that in a phenyl ring, therefore is delocalized more extensively than the latter. A better conjugation in the former is also supported by a more planar conformation. For example, the dihedral angle between adjacent aryl rings is nearly zero in **SSS** type structure, yet is significantly twisted (~36°) in the **PPP** type as estimated by molecular modeling. The molar extinction coefficients ($2–4\times10^4\ M^{-1}\ cm^{-1}$) of all compounds are not much different from each other, yet are all higher than that of the well known ruthenium dyes ($<2\times10^4\ M^{-1}\ cm^{-1}$). It is also noteworthy in Figure 2 that the absorption intensity of **1N** series compounds (dotted curves) is consistently higher than the corresponding ones in **1P** series (solid curves). This phenomenon seems to correspond well with the better performance of DSSC devices made with the former materials.

The first oxidation potentials (E_{ox}), corresponding to the HOMO level of dyes, were measured by cyclic voltammetry (CV) in THF (Fig. 3) and the results were summarized in Table 1. The LUMO levels of sensitizer were estimated by the values of E_{ox} and the 0–0 band gaps, the latter were obtained at the intersection of absorption and emission spectra. The band gap energies reduce along with the number of thiophene units, i.e., the band gaps arranged in the order of **1P-PPP** (2.77)>**1P-PSP** (2.53)≈**1P-PPS** (2.54)>**1P-PSS** (2.30)≈**1P-SSS** (2.24), and **1N-PPP** (2.78)>**1N-PSP** (2.52)≈**1N-PPS** (2.52)>**1N-PSS** (2.32)>**1N-SSS** (2.16). The oxidation waves of both **1P-SSS** and **1N-SSS** exhibit two maxima, which indicate clearly that amine π-orbital resonates significantly with the nearby thiophene π-orbital. The interaction pushes up the potential energy level of the amine donor, therefore lowers its oxidation potential. The estimated LUMO levels of all dyes are sufficiently higher than the electron injection level of TiO_2 (ca. −0.5 V), while their HOMO levels are sufficiently lower than that of electrolyte pair I^-/I_3^- (ca. 0.4 V). Such electronic structures thus ensure a favorable exothermic flow of charges throughout the photo-electronic conversion.

The electronic configurations were further examined by theoretical models implanted in Gaussian 03 program. Their molecular geometries were optimized by using B3LYP/6-31G* basis set first, then the orbitals of both ground and excited states were computed by time-dependent density functional theory (TDDFT) with B3LYP functional. According to the optimized molecular geometry, the conformation of two adjacent thiophene rings is nearly coplanar, but the orientation of two adjacent phenyl rings is twisted to ~36° due to steric hindrance (Supplementary data). As a result the electronic resonance is transmitted more efficiently through thiophene moieties than through phenyl groups. A better resonance



Scheme 1. Synthesis and structures of organic dyes. Reagents: (i) $Pd(OAc)_2$/dppf, 4,4′-dibromobiphenyl (**2**) or 1,4-dibromobenzene (**5**) or 2,5-bis(5′-bromothiophen-2′-yl)thiophene (**9**), toluene, 90 °C; (ii) (a) BuLi, triisopropylborate, THF, −78 °C; followed by $HCl_{(aq)}$, (b) $Pd(PPh_3)_4$, 4-bromobenzaldehyde (**3**) or 5-bromothiophene-2-carbaldehyde (**4**), toluene, K_2CO_3; (iii) cyanoacetic acid, NH_4OAc, AcOH, 90–100 °C; (iv) $PdCl_2(PPh_3)_2$, 2-(tributylstannyl)thiophene, DMF, 90 °C; (v) BuLi, tributyltin chloride, THF, −78 °C; followed by $PdCl_2(PPh_3)_2$, 4-bromobenzaldehyde (**7**) or 5-bromothiophene-2-cabaldehyde (**8**), DMF; (vi) (a) BuLi, THF, −78 °C (b) DMF.

along thiophene moieties leads to a lower band gaps, yet the same effect also promotes the rate of charge recombination, which quenches the excited state. The HOMO/LUMO energy levels and band gaps of the dyes are listed in Table 1.

The electronic density distributions before and after photo-excitation can be illustrated better by the graphs in Figure 4. The electron densities in the HOMOs are distributed mainly around the amine moieties (D), and those in the LUMOs around the cyanoacrylic acid moieties (A). Photo-excitation pumps an electron from the HOMO to the LUMO, therefore shifts considerable amount of electron density from D to A. The difference of Mulliken charge density surrounding D, B, and A moieties before (S_0 state) and after (S_1 state) photo-excitation was arranged in the order of magnitude (Supplementary data). The degree of charge separation declines

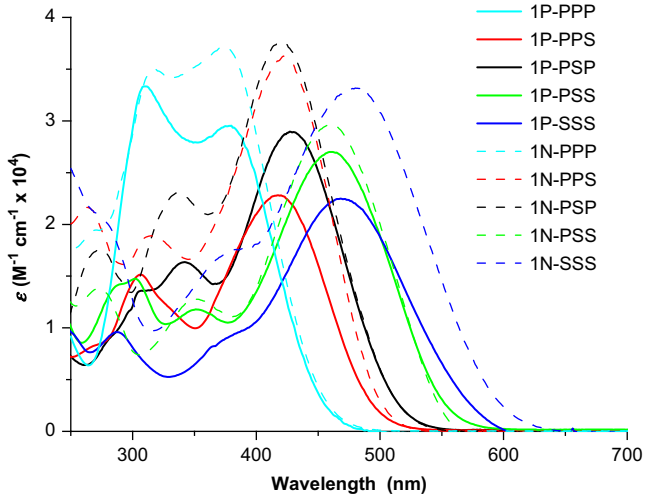


Figure 2. Absorption spectra of organic dyes in THF, where ϵ is molar extinction coefficient.

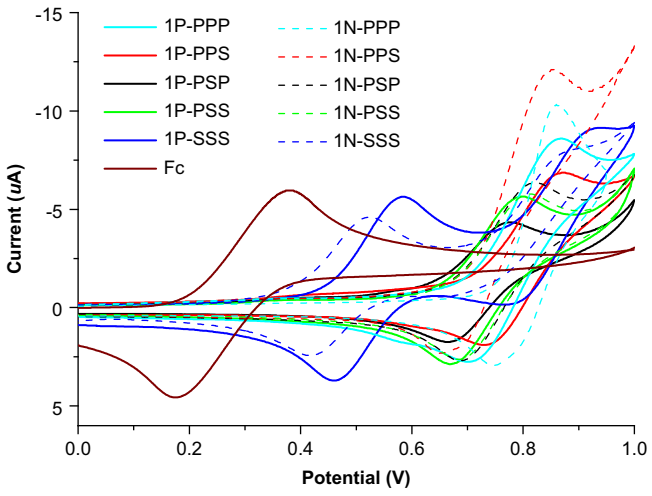


Figure 3. Oxidative voltammograms of compounds **1P**s and **1N**s.

Table 1
Calculated (TDDFT/B3LYP) and experimental parameters for dyes **1N**s and **1P**s

Dye	HOMO/LUMO[a] (eV)	Band gap[a]	f[a]	λ_{abs}[b] (nm)/(ε (M^{-1} cm^{-1}))	E_{0-0}[b] (eV)	E_{ox}[c] (V)	E_{HOMO}/E_{LUMO}[d] (V)	J_{sc} (mA cm^{-2})	V_{oc} (V)	FF	η[e] (%)
1P-PPP	−5.08/−2.57	2.50	0.28	380(30,200)	2.77	0.85	5.35/2.58	11.43	0.65	0.62	4.58
1P-PPS	−5.09/−2.64	2.45	0.41	417(23,000)	2.54	0.86	5.36/2.82	13.86	0.65	0.57	5.14
1P-PSP	−5.06/−2.61	2.45	0.71	427(29,000)	2.53	0.79	5.29/2.77	15.36	0.69	0.50	5.25
1P-PSS	−5.08/−2.69	2.38	0.85	461(27,100)	2.30	0.79	5.29/2.99	16.26	0.66	0.58	6.17
1P-SSS	−5.02/−2.72	2.29	0.96	468(22,500)	2.24	0.58	5.08/2.84	10.89	0.58	0.60	3.75
1N-PPP	−5.10/−2.59	2.51	0.26	375(37,400)	2.78	0.83	5.33/2.55	11.24	0.68	0.60	4.60
1N-PPS	−5.08/−2.60	2.48	0.44	422(36,300)	2.52	0.82	5.32/2.80	14.20	0.66	0.60	5.68
1N-PSP	−5.12/−2.63	2.49	0.77	422(37,700)	2.52	0.82	5.32/2.80	16.81	0.74	0.57	7.08
1N-PSS	−5.11/−2.70	2.41	0.83	461(31,300)	2.32	0.81	5.31/2.99	14.28	0.71	0.60	6.12
1N-SSS	−4.99/−2.69	2.30	1.03	480(22,200)	2.16	0.53	5.03/2.87	11.88	0.58	0.54	3.74
N719	—	—	—	—	—	—	—	17.68	0.75	0.61	7.64

f: Oscillator strength for the lowest energy transition; ε: absorption coefficient; E_{ox}: oxidation potential; E_{0-0}: 0–0 transition energy measured at the intersection of absorption and emission spectra; J_{sc}: short-circuit photocurrent density; V_{oc}: open-circuit photovoltage; FF: fill factor; η: total power conversion efficiency.
[a] TDDFT/B3LYP calculated values.
[b] In THF.
[c] Oxidation potential in THF (10^{-3} M) containing 0.1 M (n-$C_4H_9)_4NPF_6$ with a scan rate of 100 mV s^{-1}.
[d] E_{HOMO} was calculated by E_{ox}+4.5 V (vs NHE), and $E_{LUMO}=E_{HOMO}-E_{0-0}$.
[e] Performance of DSSC measured in a 0.25 cm^2 working area on an FTO (15 Ω/square) substrate.

along with the additional number of thiophenylene groups in the arrays, as a result of more coplanar conformation across the ring junctions. Such a phenomenon can best be demonstrated by a comparison of the HOMO and LUMO orbitals between **1P-SSS** and **1P-PPP** as shown in Figure 4. The orbitals delocalize over a wider range through the relay of thiophene groups in the former than they do through the phenylene linkages in the latter.

Typical DSSC devices with an effective area of 0.25 cm^2 were fabricated with the dyes as sensitizers, which were coated on the surface of nanocrystalline anatase TiO_2. A mixture of I_2 (0.05 M), LiI (0.5 M), and *tert*-butylpyridine (0.5 M) in acetonitrile solution was used as an electrolyte. The photovoltaic performance under a solar condition (AM 1.5) is summarized in Table 1 The *J*–*V* curves of all dyes are shown in Figure 5. The current density maintains a constant value within a range of 11–17 mA cm^{-2} up to 0.4 V. Plots of IPCE at various wavelengths are given in Figure 6. The active photo-to-current conversion area of these dyes lies in the blue/green region, as implied by their absorption spectra (Fig. 2). Nevertheless their optimal conversion ratios reach to ca. 80%, quite close to that of N719 at the same wavelengths. Generally speaking, the **1N** series compounds perform relatively better than the **1P** series compounds, that is, consistent with a higher absorptivity of **1N** series compounds than that of **1P** series compounds (Fig. 2). The naphthalene substituent may also have provided a better environment for resonance around the nitrogen donor, thus stabilizing the positive charge better. The larger size of naphthalene may also have an effect on increasing the steric hindrance to prevent the material from self-aggregation.

A comparison between the performances of **1P-SSS** and **1P-PPP** is worth mentioning. The former exhibited both a lower short-circuit current (J_{sc}=10.9 mA cm^{-2}) and a lower open-circuit voltage (V_{oc}=0.58 V) than the former (J_{sc}=11.4 mA cm^{-2}; V_{oc}=0.65 V). The overall field factor (FF) of the former (0.60) turned out slightly smaller than that of the latter (0.62), which led to a relatively lower quantum efficiency (3.75% vs 4.58%). The efficiency of DSSCs indeed depends upon a delicate balance between the degree of electronic resonance and the rate of charge recombination of an organic chromophore. Among all compounds, the best performance was found in compound **1N-PSP**. A device made of this material exhibited J_{sc} value of 16.81 mA cm^{-2}, V_{oc} value of 0.74 V, and *FF* value of 0.57. The overall conversion efficiency (η) was estimated to be 7.08%, quite compatible to the well-known ruthenium complex N719. The incident photon to current conversion efficiency (IPCE) was higher than 80% at 450–470 nm region. Besides **1N-PSP**, others like **1P-PSS**,[15] **1N-PPS**, and **1N-PSS** also yielded quantum efficiency in the proximity of 6%.

In summary, a series of dipolar compounds containing a triarylene bridge were prepared by convenient methods and can be used as highly efficient dye sensors in organic solar cells. In their structures, either a diphenylamino (type **1P**) or a naphthylphenylamino (type **1N**) group was attached to a terminal of a triarylene bridge as an electron donor, while a cyanoacrylic acid moiety on the other end as an acceptor. The triarylene bridges consist of phenyl and/or thiophenyl groups linked together in a linear fashion. These compounds exhibited a high absorptivity in the blue/green region of solar light. The DSSC devices fabricated by using these materials as dye sensors displayed remarkable quantum efficiency, typically in a range of 5–7%. The optimal IPCE value reaches beyond 80%. The performance of **1N** type compounds, in general, was slightly better than that of the **1P** type. This can be ascribed partly to the higher absorptivity of **1N** series compounds, and partly to a better resonance effect provided by a naphthalene moiety. The larger size of naphthalene group may also effectively hinder self-aggregation of the dyes on TiO_2 surface. The structure of bridges is also influential. The presence of thiophenylene units in the bridge improves coplanarity, thus promotes better resonance delocalization. As a result the band gap is reduced, yet with an expense of increasing the tendency of aggregation. The adjacent phenylene groups are twisted with large dihedral angle, nevertheless such a twisted conformation can retard the rate of charge recombination. A delicate balance needs to be tuned between charge separation and charge recombination by modifying the molecular structures. The best performance among these compounds was found in **1N-PSP**, which showed a maximal IPCE value of 82%, J_{sc} value of 16.81 mA·cm^{-2}, V_{oc} value of 0.74 V, and FF value of 0.57, that correspond to an overall conversion efficiency of 7.08%.

3. Experimental section

3.1. General information

All reactions were carried out under a nitrogen atmosphere. Solvents were distilled freshly according to standard procedures. ^1H and ^{13}C NMR spectra were recorded on a Bruker 400 MHz spectrometer. Absorption spectra were recorded on a Hewlett–Packard 8453 spectrofluorometer. The redox potentials were measured by using cyclic voltammetry on CHI 620 analyzer. Mass spectra were recorded on a VG70-250S mass spectrometer. Elementary analyses were performed on a Perkin–Elmer 2400 CHN analyzer. The starting materials diphenylamine, di-*p*-tolylamine, bis(4-methoxyphenyl)amine, *N*-naphthylaniline,

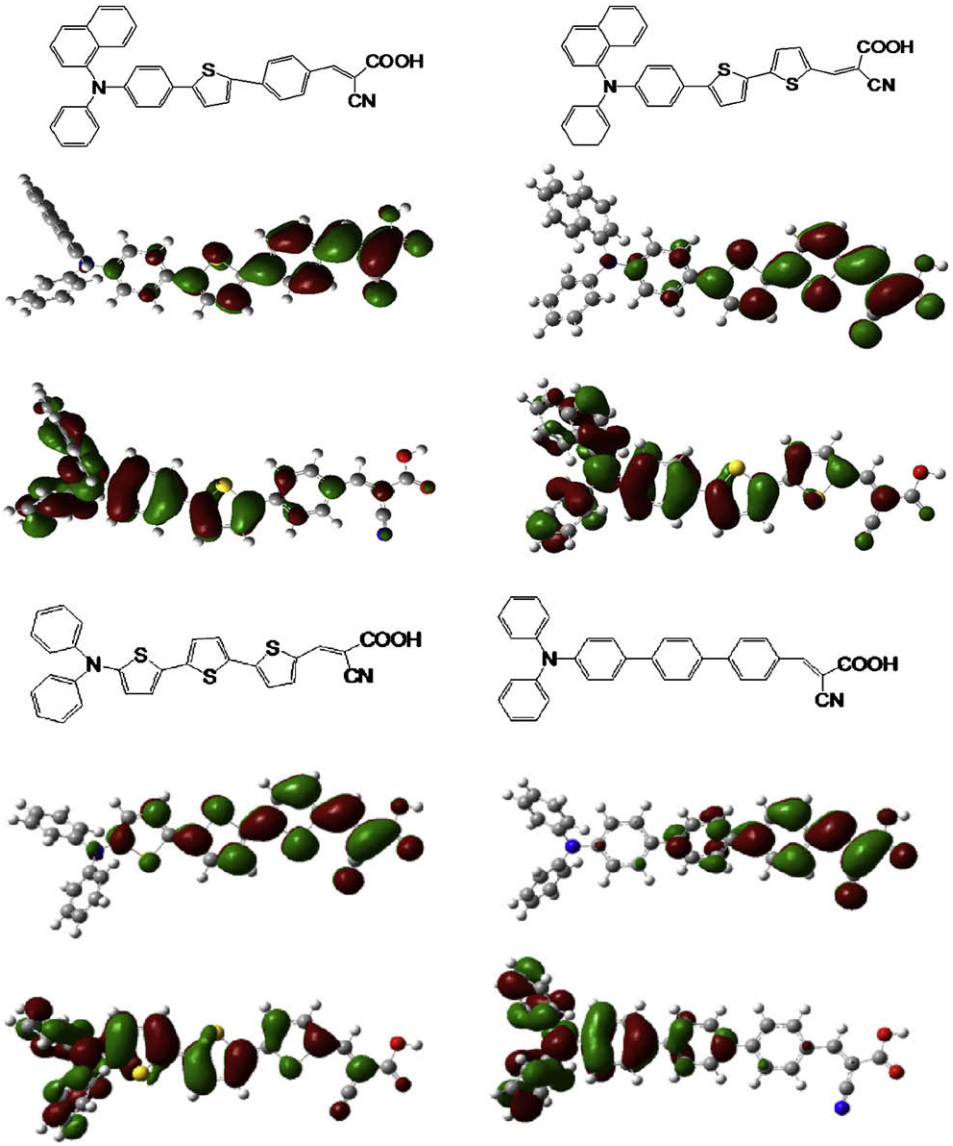


Figure 4. Computed frontier orbitals of **1N-PSP**, **1N-PSS**, **1P-SSS**, and **1P-PPP**. The upper graphs are the LUMOs and the lower ones are the HOMOs.

4,4′-dibromobiphenyl, 1,4-dibromobenzene, 4-bromobenzaldehyde, 5-bromothiophene-2-carbaldehyde, and tributyl(thiophen-2-yl)stannane were purchased from ACROS, Merck, Lancaster, TCI, Sigma–Aldrich, and purified before use. Chromatographic separations were carried out on silica gel Merk Kieselgel *si* 60 (40–63 μm).

3.2. Fabrication and characterization of DSSCs

A thin film of TiO_2 (16–18 μm thick) was coated on a 0.25 cm^2 FTO glass substrate. It was immersed in a THF solution containing 3×10^{-4} M dye sensitizers for 12 h, then rinsed with anhydrous acetonitrile and dried. Another piece of FTO with sputtering 100 nm thick Pt was used as a counter electrode. The active area was controlled at a dimension of 0.25 cm^2 by adhering 60 μm thick polyester tape on the Pt electrode. The photocathode was placed on top of the counter electrode and was tightly clipped together to form a cell. Electrolyte was then injected into the seam between two electrodes. An acetonitrile solution containing LiI (0.5 M), I_2 (0.05 M), and 4-*tert*-butylpyridine (0.5 M) was used as the electrolyte. Devices made of a commercial dye N719 under the same condition was

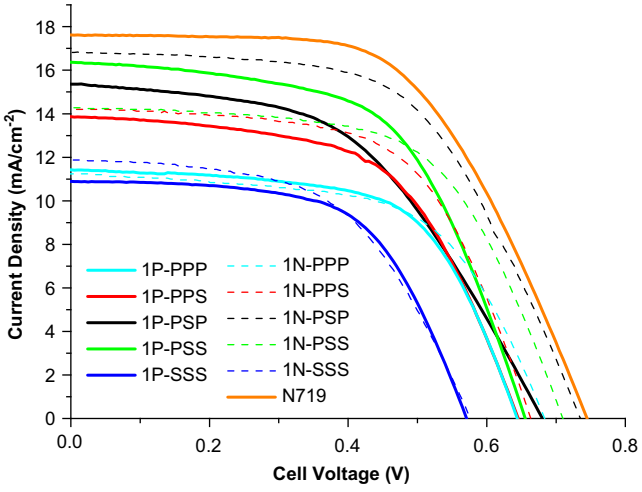


Figure 5. *I–V* curves of dyes **1N**s and **1P**s.

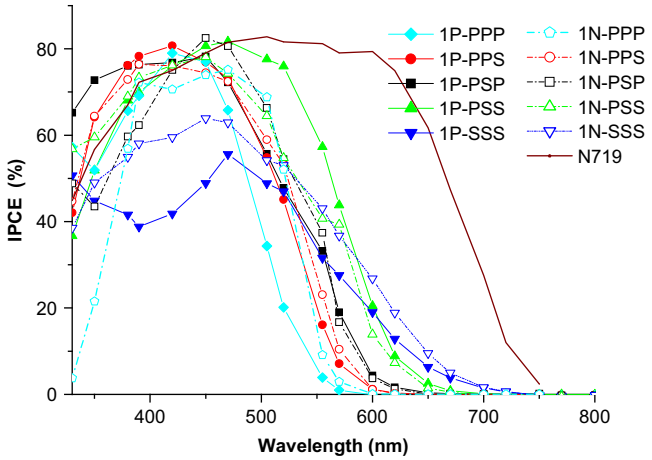


Figure 6. IPCE plots of compounds **1N**s and **1P**s.

compared as a reference. The cell parameters were obtained under an incident light with intensity 100 mW cm^{-2}, which was generated by a 300 W Xe lamp passing through an AM 1.5 filter. The current–voltage parameters of DSSCs were recorded by a potentiostat/galvanostat model CHI650B (CH Instruments, USA).

3.3. Quantum chemistry computation

The structures of dye were optimized by using B3LYP/6-31G* hybrid functional. For the excited states, a time-dependent density functional theory (TDDFT) with the B3LYP functional was employed. All analyses were performed under Q-Chem 3.0 software. The frontier orbital plots of HOMO and LUMO were drawn by using Gaussian 03.

3.4. (*E*)-2-Cyano-3-(naphthylphenylaminotriphenylene)-acrylic acid (1N-PPP)

A mixture of **3N** (242 mg, 0.51 mmol), cyanoacetic acid (52 mg, 0.61 mmol), and ammonium acetate (10 mg, 0.13 mmol) in acetic acid was placed in a three-necked flask under a nitrogen atmosphere and was stirred at 120 °C for 12 h. After cooling, the reaction was quenched by adding water and then was extracted with CH_2Cl_2. The organic layer was dried over anhydrous $MgSO_4$ and evaporated under vacuum. The products were purified by silica gel column chromatograph eluted with CH_2Cl_2/acetic acid (19/1). The orange solid was isolated in 70% yield (195 mg, 0.36 mmol), mp: 238–240 °C. *Spectroscopic data of* ***1N-PPP***. ^{1}H NMR (DMSO-d_6): δ 8.29 (s, 1H), 8.06 (d, 2H, J=8.4 Hz), 7.95 (d, 1H, J=8.2 Hz), 7.81–7.86 (m, 4H), 7.73 (d, 2H, J=8.3 Hz), 7.63 (d, 2H, J=8.3 Hz), 7.43–7.51 (m, 4H), 7.34 (t, 1H, J=7.6 Hz), 7.30 (d, 1H, J=7.2 Hz), 7.17 (t, 2H, J=7.8 Hz), 6.86–6.95 (m, 5H). ^{13}C NMR (DMSO-d_6): δ 163.8, 154.0, 148.0, 147.7, 144.2, 142.8, 140.1, 137.0, 135.3, 131.8, 130.8, 129.8, 129.0, 127.7, 127.4, 127.3, 126.9, 123.8, 122.7, 122.4, 121.1, 116.7, 103.5. HRMS (m/z): 542.1992 (M^+) (calcd for $C_{38}H_{26}N_2O_2$: 542.1994).

3.5. (*E*)-2-Cyano-3-(5′-(4″-(naphthylphenylamino)-biphenylene)thiophen-2′-yl)acrylic acid (1N-PPS)

Compound **1N-PPS** was synthesized according to the same procedure as that of **1N-PPP**. Red solid of **1N-PPS** were obtained in 65% yield, mp: 275–277 °C. ^{1}H NMR (DMSO-d_6): δ 8.36 (s, 1H), 7.94 (d, 1H, J=8.2 Hz), 7.86 (d, 1H, J=4.1 Hz), 7.84 (d, 1H, J=8.4 Hz), 7.78 (d, 1H, J=8.4 Hz), 7.67 (d, 2H, J=8.3 Hz), 7.62 (d, 1H, J=4.0 Hz), 7.57 (d, 2H, J=8.4 Hz), 7.42–7.50 (m, 4H), 7.33 (t, 1H, J=7.6 Hz), 7.27 (d, 1H, J=7.3 Hz), 7.17 (t, 2H, J=7.8 Hz), 6.90–6.94 (m, 3H), 6.83 (d, 2H, J=8.6 Hz). ^{13}C NMR (DMSO-d_6): δ 164.2, 152.3, 148.1, 147.5, 146.1, 142.7, 141.0, 140.8, 135.3, 134.9, 131.7, 131.0, 130.9, 129.8, 129.0, 127.7, 127.3, 127.1, 127.0, 126.9, 126.7, 125.1, 123.7, 122.8, 122.5, 120.9, 117.2, 99.9. HRMS (m/z): 548.1555 (M^+) (calcd for $C_{36}H_{24}N_2O_2S$: 548.1158).

3.6. (*E*)-2-Cyano-3-(*p*-(5′-(*p*-(naphthylphenylamino)-phenyl)thiophen-2′-yl)phenyl)acrylic acid (1N-PSP)

Compound **1N-PSP** was synthesized according to the same procedure as that of **1N-PPP**. Black solid of **1N-PSP** was obtained in 61% yield, mp: 260–262 °C. ^{1}H NMR (DMSO-d_6): δ 8.17 (s, 1H), 8.00 (d, 3H, J=7.7 Hz), 7.91 (d, 1H, J=8.3 Hz), 7.80–7.83 (m, 3H), 7.67 (d, 1H, J=3.9 Hz), 7.37–7.59 (m, 7H), 7.26 (t, 2H, J=7.9 Hz), 6.99–7.03 (m, 3H), 6.86 (d, 2H, J=8.7 Hz). ^{13}C NMR (DMSO-d_6): δ 164.2, 151.9, 148.2, 147.4, 145.1, 142.5, 140.2, 137.6, 135.3, 131.6, 129.8, 129.0, 127.4, 127.1, 127.0, 126.8, 125.6, 123.1, 122.7, 120.8, 117.6, 105.8. HRMS (m/z): 548.1555 (M^+) (calcd for $C_{36}H_{24}N_2O_2S$: 548.1158). Anal. Calcd for $C_{36}H_{24}N_2O_2S$: C, 78.81; H, 4.41; N, 5.11; O, 5.83; S, 5.84. Found: C, 78.77; H, 4.45; N, 5.09; O, 5.85; S, 5.84.

3.7. (*E*)-2-Cyano-3-(5′-(5″-(*p*-(naphthylphenylamino)phenyl)-thiophen-2″-yl)-thiophen-2′-yl)acrylic acid (1N-PSS)

Compound **1N-PSS** was synthesized according to the same procedure as that of **1N-PPP**. Black solids of **1N-PSS** were obtained in 67% yield, mp: 253–255 °C. ^{1}H NMR (DMSO-d_6): δ 8.28 (s, 1H), 7.98 (d, 1H, J=8.1 Hz), 7.89 (d, 1H, J=8.2 Hz), 7.78–7.81 (m, 2H), 7.54 (t, 1H, J=7.8 Hz), 7.44–7.49 (m, 5H), 7.39 (t, 1H, J=7.6 Hz), 7.33 (d, 2H, J=4.5 Hz), 7.23 (t, 2H, J=7.8 Hz), 6.96–7.01 (m, 3H), 6.81 (d, 2H, J=8.6 Hz). ^{13}C NMR (DMSO-d_6): δ 164.6, 148.4, 147.3, 145.4, 144.5, 144.3, 142.5, 139.9, 135.3, 134.5, 133.4, 130.9, 129.9, 129.0, 128.2, 127.7, 127.5, 127.2, 127.1, 126.9, 126.8, 125.8, 124.8, 124.3, 123.6, 123.2, 122.9, 120.5, 118.0, 102.7. HRMS (m/z): 554.1135 (M^+) (calcd for $C_{34}H_{22}N_2O_2S_2$: 554.1123). Anal. Calcd for $C_{34}H_{22}N_2O_2S_2$: C, 73.62; H, 4.00; N, 5.05; O, 5.77; S, 11.56. Found C, 73.59; H, 4.05; N, 5.07; O, 5.76; S, 11.53.

3.8. (*E*)-2-Cyano-3-(5′-(5″-(5‴-(naphthylphenylamino)-thiophen-2‴-yl)thiophen-2″-yl)thiophen-2′-yl)acrylic acid (1N-SSS)

Compound **1N-SSS** was synthesized according to the same procedure as that of **1N-PPP**. Black solid of **1N-SSS** was obtained in 55% yield, mp: 259–261 °C. ^{1}H NMR (DMSO-d_6): δ 8.30 (s, 1H), 7.99 (d, 1H, J=8.1 Hz), 7.93 (d, 1H, J=8.2 Hz), 7.86 (d, 1H, J=8.2 Hz), 7.78 (d, 1H, J=3.6 Hz), 7.46–7.58 (m, 4H), 7.40 (dd, 1H, J=3.8, 0.9 Hz), 7.37 (dd, 1H, J=3.8, 0.9 Hz), 7.20 (t, 2H, J=7.5 Hz), 7.09 (dd, 1H, J=3.8, 0.9 Hz), 7.06 (dd, 1H, J=3.8, 0.9 Hz), 6.93 (d, 3H, J=7.9 Hz), 6.50 (dd, 1H, J=3.9, 1.0 Hz). ^{13}C NMR (DMSO-d_6): δ 164.3, 152.5, 148.0, 145.0, 144.6, 142.4, 140.5, 138.9, 135.2, 134.4, 132.9, 130.3, 130.0, 129.8, 129.1, 128.2, 128.1, 127.5, 127.3, 127.0, 124.9, 124.6, 124.5, 123.2, 122.5, 119.4, 118.3, 117.7, 101.2. HRMS (m/z): 560.0694 (M^+) (calcd for $C_{32}H_{20}N_2O_2S_3$: 560.0687). Anal. Calcd for $C_{32}H_{20}N_2O_2S_3$: C, 68.55; H, 3.60; N, 5.00; O, 5.71; S, 17.16. Found: C, 68.60; H, 3.63; N, 4.98; O, 5.73; S, 17.15.

3.9. (*E*)-2-Cyano-3-(diphenylaminotriphenylene)acrylic acid (1P-PPP)

Compound **1P-PPP** was synthesized according to the same procedure as that of **1N-PPP**. The orange solid of **1P-PPP** was obtained in 64% yield, mp: 256–258 °C. ^{1}H NMR (DMSO-d_6): δ 8.33 (s, 1H), 8.11 (d, 2H, J=8.5 Hz), 7.92 (d, 2H, J=8.5 Hz), 7.83 (d, 2H, J=8.5 Hz), 7.73 (d, 2H, J=8.5 Hz), 7.63(d, 2H, J=6.8 Hz), 7.29 (t, 4H, J=7.0 Hz), 7.00–7.06 (m, 8H). ^{13}C NMR (DMSO-d_6): δ 163.7, 154.1,

147.4, 147.3, 144.2, 140.1, 137.2, 133.2, 131.8, 130.8, 130.0, 127.9, 127.8, 127.4, 124.7, 123.8, 123.4, 116.7, 103.4. HRMS (m/z): 492.1830 (M^+) (calcd for $C_{34}H_{24}N_2O_2$: 492.1838). Anal. Calcd for $C_{34}H_{24}N_2O_2$: C, 82.91; H, 4.91; N, 5.69; O, 6.50. Found: C, 82.87; H, 4.93; N, 5.65; O, 6.55.

3.10. (*E*)-2-Cyano-3-(5′-(diphenylaminobiphenylene)-thiophen-2′-yl)acrylic acid (1P-PPS)

Compound **1P-PPS** was synthesized according to the same procedure as that of **1N-PPP**. Black solid of **1P-PPS** was obtained in 61% yield, mp: 267–269 °C. ^{1}H NMR (DMSO-d_6): δ 8.05 (s, 1H), 7.95 (d, 2H, J=7.4 Hz), 7.80 (d, 2H, J=8.2 Hz), 7.66 (d, 1H, J=3.7 Hz), 7.59 (d, 2H, J=8.7 Hz), 7.44 (d, 1H, J=3.8 Hz), 7.31 (t, 4H, J=7.9 Hz), 7.02–7.08 (m, 6H), 6.96 (d, 2H, J=8.7 Hz). ^{13}C NMR (DMSO-d_6): δ 164.3, 148.3, 147.5, 147.1, 144.4, 140.8, 136.4, 132.0, 130.8, 130.0, 127.5, 126.9, 126.8, 125.6, 124.8, 124.6, 123.9, 123.2, 119.1. HRMS (m/z): 498.1395 (M^+) (calcd for $C_{32}H_{22}N_2O_2S$: 498.1402). Anal. Calcd for $C_{32}H_{22}N_2O_2S$: C, 77.09; H, 4.45; N, 5.62; O, 6.42; S, 6.43. Found: C, 77.13; H, 4.49; N, 5.59; O, 6.45; S, 6.34.

3.11. (*E*)-2-Cyano-3-(*p*-(5′-(*p*-diphenylamino)phenyl)-thiophen-2′-yl)phenyl)acrylic acid (1P-PSP)

Compound **1P-PSP** was synthesized according to the same procedure as that of **1N-PPP**. Black solid of **1P-PSP** was obtained in 70% yield, mp: 262–264 °C. ^{1}H NMR (DMSO-d_6): δ 8.22 (s, 1H), 7.80 (d, 1H, J=3.7 Hz), 7.77 (d, 2H, J=8.3 Hz), 7.71 (d, 2H, J=8.3 Hz), 7.67 (d, 1H, J=3.7 Hz), 7.62 (d, 2H, J=8.5 Hz), 7.30 (t, 4H, J=7.6 Hz), 6.99–7.06 (m, 8H). ^{13}C NMR (DMSO-d_6): δ 164.2, 149.1, 147.5, 147.3, 140.3, 137.6, 136.2, 133.1, 131.6, 130.0, 127.9, 127.2, 126.8, 124.9, 124.7, 123.8, 123.4, 119.1. HRMS (m/z): 498.1395 (M^+) (calcd for $C_{32}H_{22}N_2O_2S$: 498.1402). Anal. Calcd for $C_{32}H_{22}N_2O_2S$: C, 77.09; H, 4.45; N, 5.62; O, 6.42; S, 6.43. Found: C, 77.03; H, 4.51; N, 5.57; O, 6.49; S, 6.40.

3.12. (*E*)-2-Cyano-3-(5′-(5″-(*p*-(diphenylamino)phenyl)-thiophen-2″-yl)thiophen-2′-yl)acrylic acid (1P-PSS)

Compound **1P-PSS** was synthesized according to the same procedure as that of **1N-PPP**. Black solid of **1P-PSS** was obtained in 69% yield, mp: 266–268 °C. ^{1}H NMR (DMSO-d_6): δ 8.24 (s, 1H), 7.74 (d, 1H, J=3.8 Hz), 7.50 (d, 2H, J=8.4 Hz), 7.44 (d, 1H, J=3.7 Hz), 7.41 (d, 1H, J=3.8 Hz), 7.35 (d, 1H, J=3.8 Hz), 7.26 (t, 4H, J=7.2 Hz), 7.02 (t, 4H, J=7.2 Hz), 6.97 (d, 2H, J=7.5 Hz), 6.87 (d, 2H, J=7.5 Hz). ^{13}C NMR (DMSO-d_6): δ 164.7, 147.8, 147.0, 145.2, 144.4, 144.3, 139.9, 134.6, 133.7, 130.1, 128.1, 126.9, 126.8, 124.9, 124.8, 124.6, 124.1, 122.8, 118.0, 102.6. HRMS (m/z): 504.0967 (M^+) (calcd for $C_{30}H_{20}N_2O_2S_2$: 504.0966). Anal. Calcd for $C_{30}H_{20}N_2O_2S_2$: C, 71.40; H, 3.99; N, 5.55; O, 6.34; S, 12.71. Found: C, 71.38; H, 4.01; N, 5.51; O, 6.37; S, 12.73.

3.13. (*E*)-2-Cyano-3-(5′-(5″-(5‴-(diphenylamino)-thiophen-2‴-yl)thiophen-2″-yl)thiophen-2′-yl)acrylic acid (1P-SSS)

Compound **1P-SSS** was synthesized according to the same procedure as that of **1N-PPP**. Black solid of **1P-SSS** was obtained in 60% yield, mp: 253–255 °C. ^{1}H NMR (DMSO-d_6): δ 8.31 (s, 1H), 7.80 (d, 1H, J=4.1 Hz), 7.42 (d, 1H, J=4.0 Hz), 7.41 (d, 1H, J=3.9 Hz), 7.28 (t, 4H, J=3.9 Hz), 7.14 (d, 1H, J=3.93 Hz), 7.13 (d, 1H, J=3.9 Hz), 7.05–7.07 (m, 6H), 6.53 (d, 1H, J=4.0 Hz). ^{13}C NMR (DMSO-d_6): δ 164.1, 151.7, 147.1, 145.7, 145.0, 141.1, 139.0, 134.3, 130.0, 128.6, 128.3, 125.1, 124.8, 124.6, 124.4, 123.2, 120.5, 117.4, 100.0. HRMS (m/z): 510.0537 (M^+) (calcd for $C_{28}H_{28}N_2O_2S_3$: 510.0530). Anal. Calcd for $C_{28}H_{18}N_2O_2S_3$: C, 65.86; H, 3.55; N, 5.49; O, 6.27; S, 18.84. Found: C, 65.80; H, 3.60; N, 5.45; O, 6.31; S, 18.84.

3.14. 4-Bromo-4′-(naphthylphenylamino)biphenyl (2N)

A mixture of 4,4′-dibromobiphenyl (8.46 g, 27.4 mmol), $Pd(OAc)_2$ (105 mg, 0.18 mmol), dppf (253 mg, 0.46 mmol), *N*-(1-naphthyl)-aniline (2.0 g, 9.13 mmol), and sodium *tert*-butoxide (1.32 g, 13.7 mmol) in dry toluene was placed in a three-necked flask under a nitrogen atmosphere and was stirred at 90 °C for 15 h. After cooling, the reaction was quenched by adding water and then was extracted with ethyl acetate. The organic layer was dried over anhydrous $MgSO_4$ and evaporated under vacuum. The products were purified by silica gel column chromatograph eluted with hexane. White solid of **2N** was obtained in 70% yield (2.86 g, 6.37 mmol). *Spectroscopic data of **2N**.* ^{1}H NMR ($CDCl_3$): δ 7.95 (d, 1H, J=7.9 Hz), 7.90 (d, 1H, J=7.9 Hz), 7.79 (d, 1H, J=8.2 Hz), 7.44–7.52 (m, 4H), 7.35–7.41 (m, 6H), 7.20–7.24 (m, 2H), 7.03–7.11 (m, 4H), 6.97 (t, 1H, J=7.3 Hz). ^{13}C NMR ($CDCl_3$): δ 148.1, 147.9, 143.1, 139.5, 135.2, 132.5, 131.7, 131.2, 129.1, 128.4, 128.0, 127.4, 127.2, 126.6, 126.4, 126.3, 126.1, 124.1, 122.3, 122.1, 121.3, 120.6. FAB HRMS (m/z): 449.0783 (M^+) (calcd for $C_{28}H_{20}BrN$: 449.0779).

3.15. 4-Bromo-4′-diphenylaminobiphenyl (2P)

Compound **2P** was synthesized according to the same procedure as that of **2N**, giving **2P** in 80% yield as yellow solid. *Spectroscopic data for **2P**.* ^{1}H NMR ($CDCl_3$): δ 7.52 (d, 2H, J=8.6 Hz), 7.42 (dd, 4H, J=8.7, 1.3 Hz), 7.26 (dd, 4H, J=6.8, 1.8 Hz), 7.12 (dt, 6H, J=8.7, 1.8 Hz), 7.02 (d, 2H, J=7.3 Hz). ^{13}C NMR ($CDCl_3$): δ 147.5, 139.5, 133.5, 131.7, 129.3, 129.2, 128.1, 127.4, 124.5, 124.3, 123.6, 123.0, 120.8. FAB HRMS (m/z): 399.0633 (M^+) (calcd for $C_{24}H_{18}BrN$: 339.0623).

3.16. 4′-(Naphthylphenylamino)triphenylene-4-carbaldehyde (3N)

To a three-necked round-bottom flask containing **2N** (6.82 g, 15.2 mmol) was added dropwise BuLi (10 mL, 16.1 mmol, 1.6 M in hexane) in dry THF at −78 °C, after then solution was brought to 0 °C and was stirred by a magnetic bar for 30 min. The solution was cooled again to −78 °C and to it was added dropwise triisopropylborate (5.3 mL, 19.8 mmol). The reaction mixture was warmed up gradually to room temperature and was stirred overnight. To the reaction mixture was then added excess amount of 10% $HCl_{(aq)}$ (30 mL), while the mixture was stirred for another 1 h. The reaction was quenched by pouring into distilled water, followed by extraction with ethyl acetate. The organic layer was dried over anhydrous $MgSO_4$. Evaporation of the solvent gave a crude product, which was immediately subjected to the next reaction. It was mixed with *p*-bromobenzaldehyde (2.57 g, 14.0 mmol), $K_2CO_{3(aq)}$ (2.76 g, 2 mmol) in 10 mL H_2O, and $Pd(PPh_3)_4$ (807 mg, 0.69 mmol) in dry toluene/THF (2/1). The mixture was heated to 90 °C for 12 h. After cooling, the products were extracted with ethyl acetate and the organic layer dried over anhydrous $MgSO_4$. The crude product was dried in vacuo, and was purifies by silica gel column chromatograph eluted with CH_2Cl_2/hexane (1/1). Yellow solid of **3N** was obtained in 88% yield (6.35 g, 13.4 mmol). *Spectroscopic data for **3N**.* ^{1}H NMR ($CDCl_3$): δ 10.04 (s, 1H), 7.93–7.95 (m, 3H), 7.88 (d, 1H, J=8.1 Hz), 7.78 (t, 3H, J=6.9 Hz), 7.67 (d, 2H, J=8.6 Hz), 7.64 (d, 2H, J=8.6 Hz), 7.44–7.50 (m, 4H), 7.35–7.38 (m, 2H), 7.24 (d, 1H, J=4.2 Hz), 7.21 (d, 2H, J=7.2 Hz), 7.10 (d, 2H, J=8.6 Hz), 7.07 (d, 2H, J=8.6 Hz), 6.96 (t, 1H, J=7.2 Hz); ^{13}C NMR ($CDCl_3$): δ 191.7, 148.2, 148.0, 146.6, 143.3, 140.8, 137.6, 135.3, 135.1, 132.8, 131.3, 130.3, 129.2, 128.5, 127.7, 127.6, 127.3, 127.0, 126.7, 126.4, 124.5, 124.2, 122.4, 122.3, 121.5. FAB HRMS (m/z): 475.1933 (M^+) (calcd for $C_{35}H_{25}NO$: 475.1936).

3.17. 4′-(Diphenylamino)triphenylene-4-carbaldehyde (3P)

Compound **3P** was synthesized according to the same procedure as that of **3N**, giving **3P** in 90% yield as yellow solid. *Spectroscopic data for **3P**.* ^{1}H NMR ($CDCl_3$): δ 10.62 (s, 1H), 7.96 (d, 2H, J=8.2 Hz),

7.80 (d, 2H, *J*=8.2 Hz), 7.67–7.72 (m, 4H), 7.52 (d, 2H, *J*=8.6 Hz), 7.25–7.31 (m, 5H), 7.14–7.17 (m, 5H), 7.02 (t, 2H, *J*=7.3 Hz). ^{13}C NMR ($CDCl_3$): δ 191.8, 147.6, 147.5, 146.6, 140.7, 137.8, 135.0, 133.8, 130.2, 129.2, 127.6, 127.3, 127.0, 124.5, 123.6, 123.0. FAB HRMS (*m*/*z*): 426.1859 (M^+) (calcd for $C_{31}H_{23}NO$: 426.1858).

3.18. 5-(Naphthylphenylamino)biphenylenethiophene-2-carbaldehyde (4N)

Compound **4N** was synthesized according to the same procedure as that of **3N**, giving **4N** in 80% yield as yellow solid. *Spectroscopic data for **4N***. ^{1}H NMR ($CDCl_3$): δ 9.88 (s, 1H), 7.98 (d, 1H, *J*=8.4 Hz), 7.91 (d, 1H, *J*=8.2 Hz), 7.81 (d, 1H, *J*=8.2 Hz), 7.71 (d, 1H, *J*=4.0 Hz), 7.69 (d, 2H, *J*=8.4 Hz), 7.59 (d, 2H, *J*=8.4 Hz), 7.36–7.52 (m, 7H), 7.22–7.26 (m, 2H), 7.13 (d, 2H, *J*=7.6 Hz), 7.07 (d, 2H, *J*=8.6 Hz), 7.00 (t, 1H, *J*=7.3 Hz). ^{13}C NMR ($CDCl_3$): δ 182.6, 154.1, 148.3, 147.9, 143.1, 142.1, 141.6, 137.4, 135.3, 132.3, 131.2, 131.1, 129.2, 128.4, 127.4, 127.3, 126.9, 126.7, 126.5, 126.3, 126.2, 124.1, 123.7, 122.5, 122.3, 121.2. FAB HRMS (*m*/*z*): 481.1505 (M^+) (calcd for $C_{33}H_{23}NOS$: 481.1500).

3.19. 5-(Diphenylaminobiphenylene)thiophene-2-carbaldehyde (4P)

Compound **4P** was synthesized according to the same procedure as that of **3N**, giving yellow solid of **4P** in 88% yield. ^{1}H NMR ($CDCl_3$): δ 9.89 (s, 1H), 7.74 (d, 1H, *J*=3.9 Hz), 7.72 (d, 2H, *J*=8.4 Hz), 7.63 (d, 2H, *J*=8.4 Hz), 7.50 (d, 2H, *J*=8.6 Hz), 7.42 (d, 1H, *J*=3.9 Hz), 7.25–7.30 (m, 4H), 7.13–7.15 (m, 6H), 7.05 (t, 2H, *J*=7.3 Hz). ^{13}C NMR ($CDCl_3$): δ 182.0, 154.0, 147.7, 147.4, 142.1, 141.6, 137.4, 133.3, 131.3, 129.3, 127.5, 127.1, 126.7, 124.6, 123.8, 123.4, 123.1. FAB HRMS (*m*/*z*): 431.1349 (M^+) (calcd for $C_{29}H_{21}NOS$: 431.1344).

3.20. *p*-Bromo-*N*-naphthyl-*N*-phenylaniline (5N)

Compound **5N** was synthesized according to the same procedure as that of **2N**, giving white solid of product **5N** in 65%. ^{1}H NMR ($CDCl_3$): δ 7.86 (d, 2H, *J*=9.17 Hz), 7.76 (d, 1H, *J*=8.1 Hz), 7.45 (t, 2H, *J*=7.8 Hz), 7.34 (t, 1H, *J*=7.8 Hz), 7.28 (d, 1H, *J*=7.3 Hz), 7.16–7.25 (m, 4H), 7.02 (d, 2H, *J*=7.7 Hz), 6.94 (t, 1H, *J*=7.3 Hz), 6.84 (dt, 2H, *J*=8.9, 2.6 Hz). ^{13}C NMR ($CDCl_3$): δ 147.8, 147.5, 142.9, 135.2, 131.9, 130.9, 129.2, 128.4, 127.1, 126.7, 126.5, 126.3, 126.2, 123.9, 122.7, 122.3, 122.2, 113.5. FAB HRMS (*m*/*z*): 373.0475 (M^+) (calcd for $C_{22}H_{16}BrN$: 373.0466).

3.21. *p*-Bromo-*N*,*N*-diphenylaniline (5P)

Compound **5P** was synthesized according to the same procedure as that of **2N**, giving white solid of product **5P** in 65% yield. ^{1}H NMR ($CDCl_3$): δ 7.32 (t, 2H, *J*=8.8 Hz), 7.20–7.29 (m, 4H), 7.05 (t, 4H, *J*=7.3 Hz), 6.96–7.02 (m, 2H), 6.90–6.93 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 147.3, 146.9, 132.1, 129.3, 125.0, 124.3, 123.1, 114.7. FAB HRMS (*m*/*z*): 323.0309 (M^+) (calcd for $C_{18}H_{14}BrN$: 323.0310).

3.22. *N*-Naphthyl-*N*-phenyl-*p*-(2′-thiophenyl)aniline (6N)

To a three-necked flask containing a mixture of **5N** (2.3 g, 6.19 mmol), $PdCl_2(PPh_3)_2$ (0.13 g, 0.18 mmol), and 2-tributylstannylthiophene (5.3 mL, 14.2 mmol) was added DMF (20 mL). The reaction mixture was stirred at 90 °C for 24 h. After cooling, the reaction was quenched by adding MeOH and $KF_{(aq)}$ (saturated 15 mL). The mixture was extracted with CH_2Cl_2 and the organic layer dried over anhydrous $MgSO_4$. Evaporation of the solvent gave the crude, which was purified by silica gel with hexane as eluent. The white solid in 78% yield (1.82 g, 4.82 mmol). *Spectroscopic data for **6N***. ^{1}H NMR ($CDCl_3$): δ 7.93 (d, 1H, *J*=8.2 Hz), 7.88 (d, 1H, *J*=8.2 Hz), 7.78 (d, 1H, *J*=8.2 Hz), 7.33–7.49 (m, 6H), 7.17–7.23 (m, 4H), 6.94–7.08 (m, 6H). ^{13}C NMR ($CDCl_3$): δ 148.0, 147.8, 144.3, 143.1, 135.2, 131.1, 129.1, 128.3, 127.8, 127.1, 126.6, 126.5, 126.4, 126.3, 124.1, 123.7, 122.2, 122.0, 121.9, 121.4. FAB HRMS (*m*/*z*): 377.1212 (M^+) (calcd for $C_{26}H_{19}NS$: 377.1204).

3.23. *N*,*N*-Diphenyl-*p*-(2′-thiophenyl)aniline (6P)

Product **6P** was synthesized according to the procedure as **6N**, giving a white solid of product **6P** in 80%. *Spectroscopic data for **6P***. ^{1}H NMR ($CDCl_3$): δ 7.46 (d, 2H, *J*=8.6 Hz), 7.25 (d, 2H, *J*=7.5 Hz), 7.24 (d, 2H, *J*=7.4 Hz), 7.19–7.21 (m, 2H), 7.10 (d, 4H, *J*=7.5 Hz), 7.05 (d, 2H, *J*=8.4 Hz), 7.00–7.03 (m, 3H). ^{13}C NMR ($CDCl_3$): δ 147.4, 147.1, 144.2, 129.2, 128.5, 127.9, 126.6, 124.4, 123.9, 123.7, 122.9, 122.1. FAB HRMS (*m*/*z*): 327.1084 (M^+) (calcd for $C_{22}H_{17}NS$: 327.1082).

3.24. *p*-(5-(*p*-(Naphthylphenylamino)phenyl)thiophen-2-yl)benzaldehyde (7N)

To a three-necked flask containing a mixture of **6N** (4.67 g, 12.4 mmol) in dry THF was adding dropwise BuLi (10 mL, 16.1 mmol, 1.6 M in hexane) at −78 °C, then the solution was allowed to warm up gradually to 0 °C for ca. 30 min. The solution was cooled again to −78 °C and to it was added dropwise tri-*n*-butylchlorostannane (5.3 mL, 16.1 mmol). The reaction mixture was warmed up to room temperature and stirred overnight. The reaction mixture was quenched by the addition of water, and was extracted with CH_2Cl_2. The combined organic solution was dried over anhydrous $MgSO_4$ and dried in vacuo. The crude product was dissolved in dry DMF, to which were added *p*-bromobenzaldehyde (2.28 g, 12.38 mmol) and $PdCl_2(PPh_3)_2$ (237 mg, 0.37 mmol). The solution was heated to 90 °C for 24 h and then cooled. The reaction was quenched by the addition of MeOH and $KF_{(aq)}$ (saturated 15 mL). The mixture was extracted with CH_2Cl_2, while the organic layer was dried over anhydrous $MgSO_4$. Evaporation of the solvent gave a product, which was purified by silica gel column chromatograph eluted with CH_2Cl_2/hexane (1/1). Compound **7N** was obtained in 75% yield (4.47 g, 9.3 mmol) as white solid. *Spectroscopic data for **7N***. ^{1}H NMR ($CDCl_3$): δ 9.97 (s, 1H), 7.91 (d, 1H, *J*=8.6 Hz), 7.88 (d, 1H, *J*=7.8 Hz), 7.84 (d, 2H, *J*=8.4 Hz), 7.78 (d, 1H, *J*=8.2 Hz), 7.72 (d, 2H, *J*=8.2 Hz), 7.34–7.49 (m, 7H), 6.96–7.23 (m, 8H). ^{13}C NMR ($CDCl_3$): δ 191.3, 148.4, 147.7, 146.1, 142.9, 140.3, 140.1, 135.2, 134.7, 131.1, 130.4, 129.2, 128.4, 127.3, 126.8, 126.6, 126.5, 126.4, 126.3, 126.2, 126.0, 125.4, 124.0, 123.1, 122.6, 122.5, 121.0. FAB HRMS (*m*/*z*): 481.1498 (M^+) (calcd for $C_{33}H_{23}NOS$: 481.1500).

3.25. *p*-(5-(*p*-(Diphenylamino)phenyl)thiophen-2-yl)-benzaldehyde (7P)

Product **7P** was synthesized according to the procedure as **7N**, giving a white solid of product **7P** in 78%. *Spectroscopic data for **7P***. ^{1}H NMR ($CDCl_3$): δ 10.00 (s, 1H), 7.89 (d, 2H, *J*=8.5 Hz), 7.76 (d, 2H, *J*=8.3 Hz), 7.51 (d, 2H, *J*=8.7 Hz), 7.43 (d, 1H, *J*=3.8 Hz), 7.27–7.31 (m, 4H), 7.24 (d, 1H, *J*=3.8 Hz), 7.05–7.10 (m, 8H). ^{13}C NMR ($CDCl_3$): δ 191.3, 147.8, 147.2, 145.9, 140.61, 140.1, 134.8, 130.4, 129.3, 127.5, 126.5, 126.0, 125.4, 124.6, 123.4, 123.3, 123.2. FAB HRMS (*m*/*z*): 431.1342 (M^+) (calcd for $C_{29}H_{21}NOS$: 431.1344).

3.26. 5-(5′-(*p*-(Naphthylphenylamino)phenyl)thiophen-2′-yl)thiophene-2-carbaldehyde (8N)

Compound **8N** was synthesized according to the same procedure as that of **7N**, giving orange solid of **8N** in 68% yield. ^{1}H NMR ($CDCl_3$): δ 9.82 (s, 1H), 7.97 (d, 1H, *J*=8.4 Hz), 7.92 (d, 1H, *J*=8.2 Hz), 7.82 (d, 1H, *J*=8.2 Hz), 7.57 (d, 1H, *J*=4.0 Hz), 7.46–7.51 (m, 4H), 7.36–7.40 (m, 4H), 7.26 (d, 1H, *J*=4.0 Hz), 7.24 (d, 2H, *J*=7.8 Hz), 7.16 (d, 1H,

J=4.0 Hz), 7.14 (d, 2H, *J*=7.6 Hz), 7.08 (d, 1H, *J*=3.9 Hz), 7.03 (d, 1H, *J*=7.3 Hz), 6.98 (d, 2H, *J*=8.7 Hz). ^{13}C NMR ($CDCl_3$): δ 182.3, 148.6, 147.4, 146.3, 142.9, 141.1, 137.4, 135.3, 133.7, 131.1, 129.3, 128.5, 127.3, 127.2, 126.9, 126.6, 126.5, 126.4, 126.3, 126.1, 124.0, 123.6, 122.9, 122.8, 122.7, 120.9. FAB HRMS (*m*/*z*): 487.1068 (M^+) (calcd for $C_{31}H_{21}NOS_2$: 487.1065).

3.27. 5-(5′-(*p*-Diphenylaminophenyl)thiophen-2′-yl)-thiophene-2-carbaldehyde (8P)

Compound **8P** was synthesized according to the same procedure as that of **7N**, giving yellow solid of **8P** in 68% yield. ^{1}H NMR ($CDCl_3$): δ 9.84 (s, 1H), 7.65 (d, 1H, *J*=3.9 Hz), 7.45 (d, 2H, *J*=8.3 Hz), 7.22–7.31 (m, 6H), 7.04–7.17 (m, 9H). ^{13}C NMR ($CDCl_3$): δ 182.3, 148.0, 147.3, 147.2, 146.2, 141.2, 137.1, 134.0, 129.3, 127.1, 127.0, 126.5, 124.7, 123.6, 123.4, 123.1, 123.0. FAB HRMS (*m*/*z*): 437.0912 (M^+) (calcd for $C_{27}H_{19}NOS_2$: 437.0809).

3.28. 5-(5′-(5″-Bromothiophen-2″-yl)thiophen-2′-yl)-2-(naphthylphenylamino)thiophene (9N)

Compound **9N** was synthesized according to the same procedure as that of **2N**, giving yellow solid of **9N** in 47% yield. ^{1}H NMR ($CDCl_3$): δ 8.02 (d, 1H, *J*=8.3 Hz), 7.86 (d, 1H, *J*=8.2 Hz), 7.42–7.52 (m, 4H), 7.21 (t, 2H, *J*=7.9 Hz), 7.04 (d, 2H, *J*=8.2 Hz), 6.85–6.97 (m, 6H), 6.52 (d, 1H, *J*=4.0 Hz). ^{13}C NMR ($CDCl_3$): δ 151.8, 148.5, 142.8, 138.7, 137.2, 135.1, 134.0, 130.7, 130.6, 129.0, 128.4, 127.4, 126.7, 126.4, 126.3, 126.2, 125.7, 124.4, 123.8, 123.6, 123.0, 122.4, 121.6, 119.1, 118.5, 117.8, 110.6. FAB HRMS (*m*/*z*): 542.9774 (M^+) (calcd for $C_{28}H_{18}BrNS_3$: 542.9785).

3.29. 5-(5′-(5″-Bromothiophen-2″-yl)thiophen-2′-yl)-2-diphenylaminothiophene (9P)

Compound **9P** was synthesized according to the same procedure as that of **2N**, giving yellow solid of **9P** in 50% yield. ^{1}H NMR ($CDCl_3$): δ 7.24–7.27 (m, 4H), 7.14–7.16 (m, 4H), 7.03 (t, 2H, *J*=7.3 Hz), 6.94 (d, 1H, *J*=3.8 Hz), 6.93 (d, 1H, *J*=3.8 Hz), 6.91 (d, 1H, *J*=3.8 Hz), 6.89 (d, 1H, *J*=3.8 Hz), 6.85 (d, 1H, *J*=3.8 Hz), 6.55 (d, 1H, *J*=3.8 Hz). ^{13}C NMR ($CDCl_3$): δ 151.0, 147.4, 138.6, 137.1, 134.2, 130.6, 130.3, 129.2, 124.4, 123.4, 123.3, 123.2, 122.7, 122.4, 120.7, 110.7. FAB HRMS (*m*/*z*): 492.9628 (M^+) (calcd for $C_{24}H_{16}BrNS_3$: 492.9628).

3.30. 5-(5′-(5″-(Naphthylphenylamino)thiophen-2″-yl)-thiophen-2′-yl)thiophene-2-carbaldehyde (10N)

To a three-necked flask containing a solution of **9N** (0.94 g, 1.73 mmol) in dry THF was added dropwise BuLi (1.6 mL, 2.6 mmol, 1.6 M in hexane) at −78 °C. The solution was allowed to warm up gradually to 0 °C for about 30 min. The solution was cooled again to −78 °C, then to it was added dropwise DMF (0.2 mL, 2.6 mmol). The reaction mixture was warmed up to room temperature and was stirred with a magnetic bar for overnight. The reaction was quenched by the addition of distilled water, and then was extracted with CH_2Cl_2. The organic layers were combined and dried over anhydrous $MgSO_4$. The solvent was evaporated in vacuo to yield crude product, which was purified by silica gel column chromatograph eluted with CH_2Cl_2/hexane (1/1). Compound **10P** was obtained as yellow solid in 72% yield (0.61 g, 1.24 mmol). *Spectroscopic data for* ***10N***. ^{1}H NMR ($CDCl_3$): δ 9.82 (s, 1H), 8.01 (d, 1H, *J*=8.2 Hz), 7.91 (d, 1H, *J*=8.0 Hz), 7.83 (d, 1H, *J*=7.6 Hz), 7.61 (d, 1H, *J*=4.0 Hz), 7.43–7.53 (m, 4H), 7.14–7.25 (m, 4H), 7.06–7.08 (m, 2H), 6.93–6.98 (m, 2H), 6.88 (d, 1H, *J*=3.9 Hz), 6.49 (d, 1H, *J*=3.9 Hz). ^{13}C NMR ($CDCl_3$): δ 182.2, 152.8, 148.3, 147.0, 142.8, 141.2, 139.8, 137.3, 135.1, 133.2, 130.6, 129.1, 128.4, 127.8, 127.5, 126.9, 126.8, 126.4, 126.3, 126.2, 123.6, 123.5, 123.3, 123.2, 121.9, 119.5, 117.8. FAB HRMS (*m*/*z*): 493.0620 (M^+) (calcd for $C_{29}H_{19}NOS_3$: 493.0629).

3.31. 5-(5′-(5″-(Diphenylamino)thiophen-2″-yl)thiophen-2′-yl)thiophene-2-carbaldehyde (10P)

Compound **10P** was synthesized according to the same procedure as that of **10N**, giving yellow solid of **10P** in 60% yield. ^{1}H NMR ($CDCl_3$): δ 9.81 (s, 1H), 7.60 (d, 1H, *J*=4.0 Hz), 7.26–7.29 (m, 4H), 7.15–7.19 (m, 6H), 7.0 (t, 2H, *J*=7.3 Hz), 6.97 (d, 1H, *J*=3.6 Hz), 6.93 (d, 1H, *J*=3.8 Hz), 6.55 (d, 1H, *J*=3.8 Hz). ^{13}C NMR ($CDCl_3$): δ 182.2, 152.0, 147.4, 146.9, 141.3, 139.7, 137.3, 133.5, 129.3, 123.8, 123.7, 123.6, 123.0, 120.1. FAB HRMS (*m*/*z*): 443.0472 (M^+) (calcd for $C_{25}H_{17}NOS_3$: 443.0472).

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Supplementary data

Solvent-dependent absorption spectra of **1P**-**PSP** and **1P**-**SSS**, TDDFT calculated orbitals, Mulliken charges, and low energy transitions of selected compounds, ^{1}H and ^{13}C NMR spectra of all compounds. Supplementary data associated with this article can be found in the online version at doi:10.1016/j.tet.2009.04.024.

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