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Ferrocenyl substituted triphenylamine based donor–acceptor molecular systems; synthesis, photophysical, electrochemical, and theoretical studies

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ABSTRACT

A series of push–pull molecular systems **5**–**14** were designed, and synthesized by the Sonogashira cross-coupling, Knoevenagel condensation, and cycloaddition reactions. The donor 'ferrocenyl substituted triphenylamine' was kept constant, whereas the acceptors were varied (malononitrile, indanone, and tetralone). The electronic absorption spectra of the ferrocenyl substituted triphenylamine based donor–acceptor (D–A) compounds **5**–**9** exhibit intense intramolecular charge transfer (ICT) band in the visible region (415–502 nm). The incorporation of the tetracyanoethylene (TCNE) group in compounds **5**–**9** results in new D–A system **10**–**14**, which exhibits the ICT band in the region 630–700 nm. The electrochemical studies suggest considerable donor–acceptor interaction. The computational studies reveal strong D–A interaction, and show good agreement with the experimental results.

1. Introduction

There has been increasing interest in the design, and synthesis of push–pull molecular systems because of their applications in nonlinear optics (NLO), and organic photovoltaics (OPV).[1,2] In push–pull systems the electron donating group is attached to the electron accepting group via π-conjugated spacer (D–π–A). The photonic properties of the push–pull systems can be tuned by varying the strength of donor/acceptor groups, and the π-spacer.[3]

Our group is interested in the design, and synthesis of push–pull systems for variety of applications.[4] We have explored ferrocene as a strong electron donor.[5] The triphenylamine (TPA) moiety is also a strong electron donor.[6] Therefore attaching the ferrocene unit on the periphery of the triphenylamine will increase its donor strength.

Francois Diederich has explored tetracyanoethylene (TCNE), as a strong electron acceptor.[7] TCNE undergo rapid [2+2] cycloaddition followed by electrocyclic ring opening with electron donating acetylenes, and exhibit intramolecular charge transfer.[8]

Triphenylamine based donor–acceptor systems have been widely studied for organic photovoltaic devices. To the best of our knowledge, there are no reports, where ethynyl ferrocene substituted triphenylamine is attached with the acceptor. In this article we report synthesis, photophysical, electrochemical, and computational properties of the ferrocenyl substituted triphenylamine based donor connected to the acceptors; malononitrile (a), indan-1,3-dione (b), 1-indanone (c), 1-tetralone (d), tetracyanoethylene (e).

2. Results and discussion

The ferrocenyl substituted triphenylamine based donor–acceptor molecular systems **5**–**14** (Chart 1), were designed, and synthesized by the Pd-catalyzed Sonogashira cross-coupling, Knoevenagel condensation, and cycloaddition reactions.

The triphenylamine based intermediate **2** was synthesized by the Vilsmeier–Haack formylation reaction of triphenylamine **1**.[9] The monoformylation reaction selectively occurred at the *para*-position of the phenyl ring, which resulted 4-(diphenylamino)-benzaldehyde **2** in 80% yield. The iodination reaction of **2** in the presence of potassium iodide (KI), potassium iodate (KIO_3), and acetic acid as a solvent resulted 4-(bis(4-iodophenyl)amino)-benzaldehyde **3** in 85% yield (Scheme 1).[10]

The Pd-catalyzed Sonogashira cross-coupling reaction of **3** (4-(bis-(4-iodophenyl)-amino]-benzaldehyde) with ethynyl ferrocene resulted mono substituted **4**, and di-substituted ferrocenyl triphenylamine aldehyde **5** in 20% and 65% yields, respectively (Scheme 2).

The ferrocenyl substituted triphenylamine based donor–acceptor compounds **6**–**9** were synthesized by the Knoevenagel condensation reaction of compound **5**, with the corresponding active methylene compounds; malononitrile (a), indan-1,3-dione (b), 1-indanone (c),

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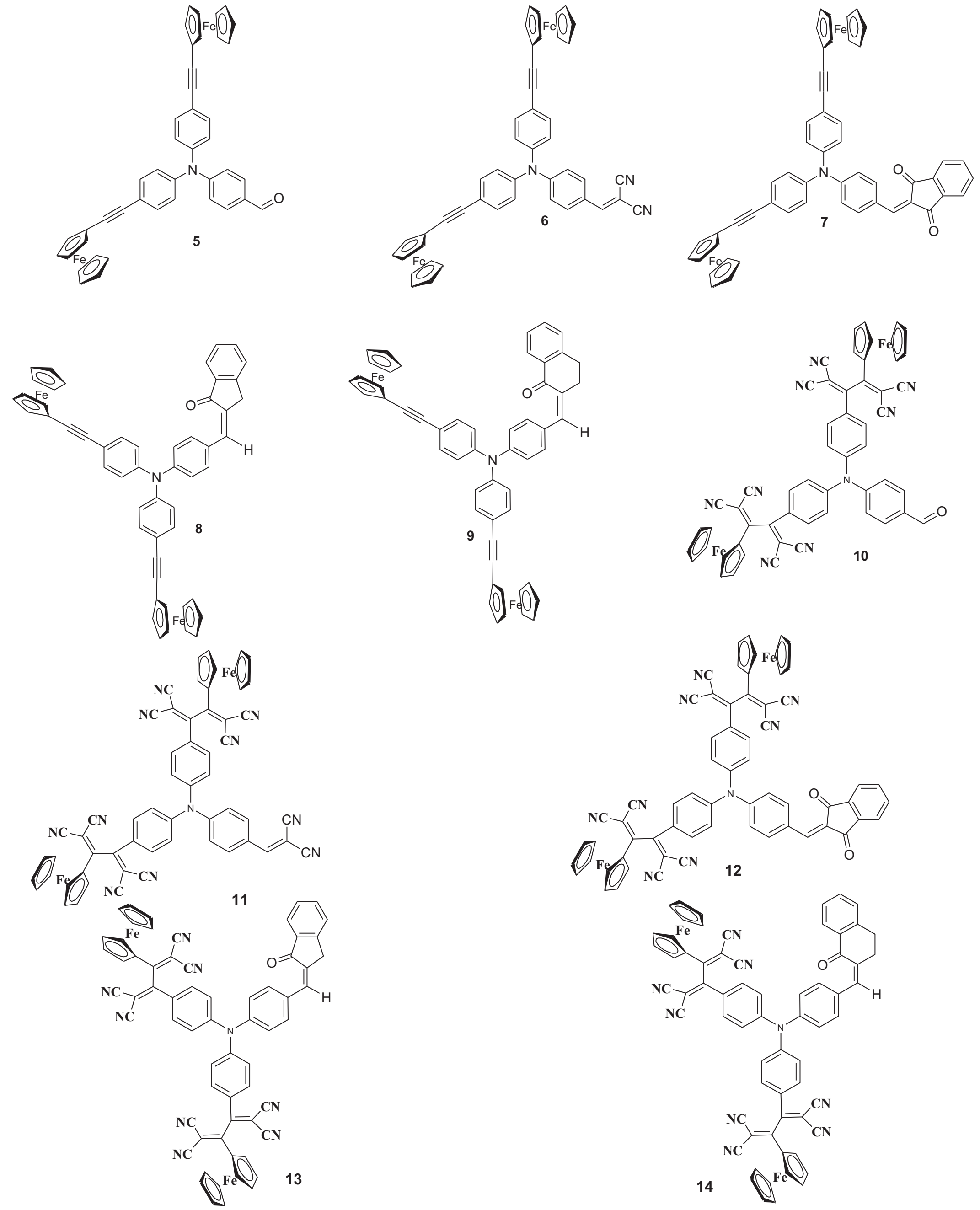
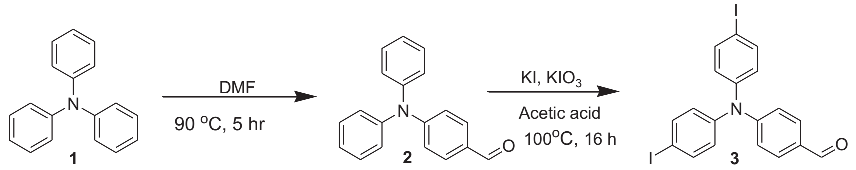
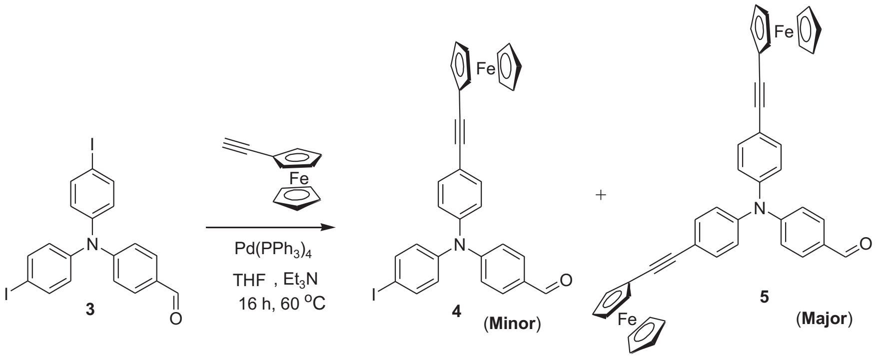


Chart 1. Molecular structures of the ferrocenyl substituted triphenylamine based donor–acceptor compounds **5**–**14**.

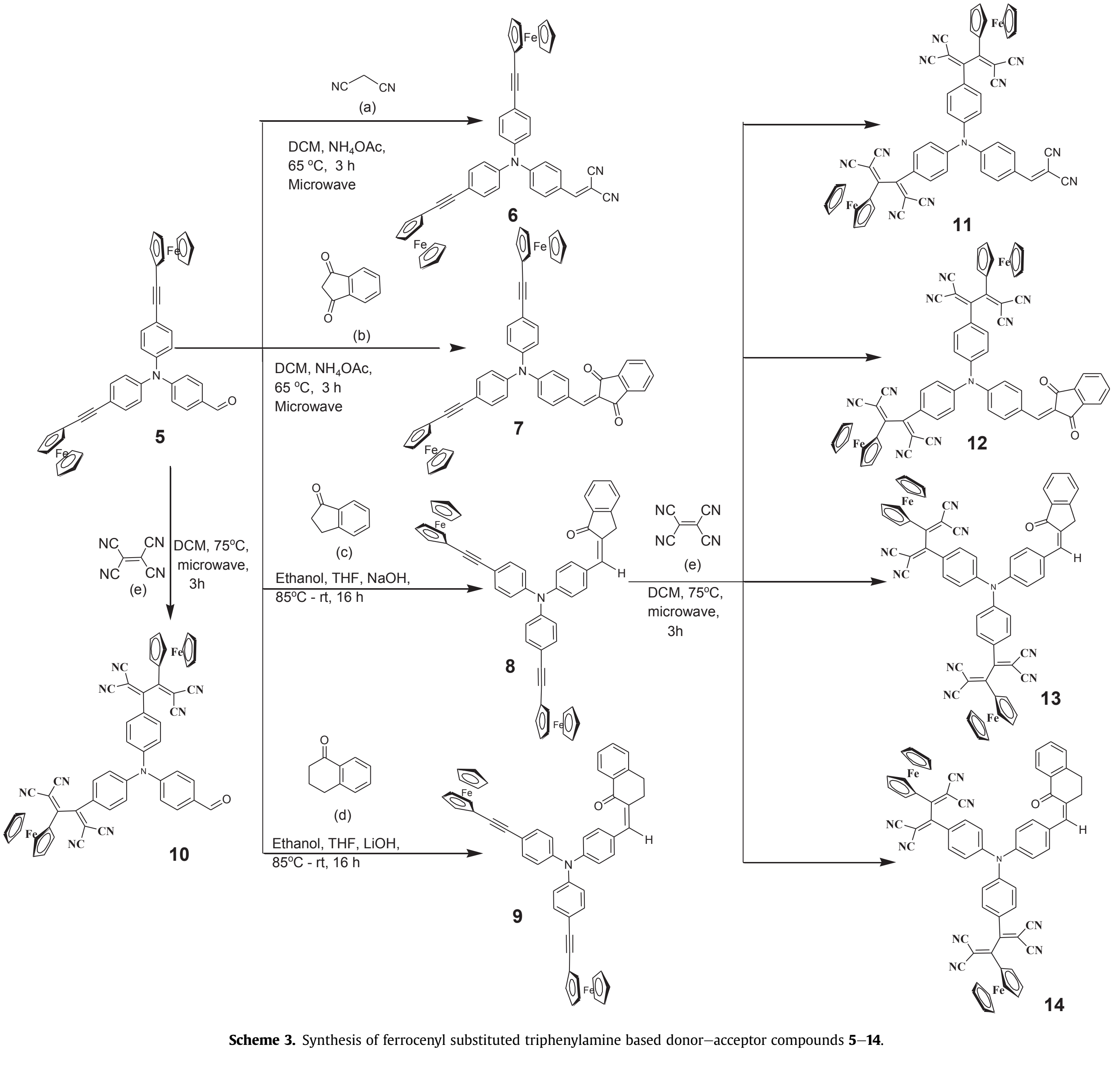


Scheme 1. Synthesis of compounds **2**–**3**.

1-tetralone (d). The Knoevenagel condensation reaction of compound **5**, with malononitrile (a), and indan-1,3-dione (b) in dichloromethane, and NH$_4$OAC as a base in microwave at 65 °C resulted **6** and **7** in 85% and 80% yields, respectively. The condensation reaction of **5** with 1-indanone (c), and 1-tetralone (d) in ethanol and THF (3:1) as solvent under basic condition resulted, ferrocenyl substituted triphenylamine based donor–acceptor compounds **8** and **9** in 75% and 70% yields, respectively. The [2+2] cycloaddition reaction of donor–acceptor compounds **5**–**9** with tetracyanoethylene (TCNE) at 75 °C, in dichloromethane solvent in microwave resulted compounds **10**–**14** in 60–72% yield (Scheme 3).



Scheme 2. Synthesis of aldehydes **4** and **5**.



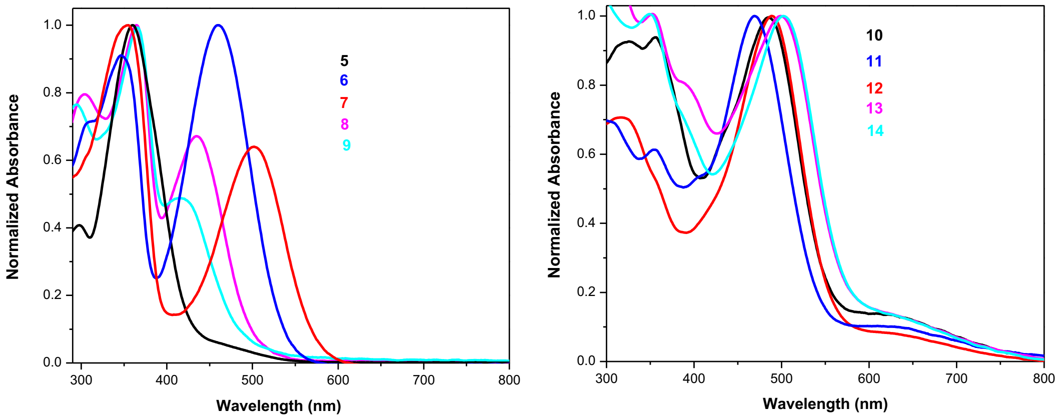
Scheme 3. Synthesis of ferrocenyl substituted triphenylamine based donor–acceptor compounds **5**–**14**.

The ferrocenyl substituted triphenylamine based donor–acceptor compounds **5**–**14** were found to be stable in solid, and solution phase. All the compounds were well characterized by UV–vis absorption, ^{1}H NMR, ^{13}C NMR, and HRMS techniques. The typical ^{1}H NMR spectrum of the donor–acceptor compounds **6**–**9** show following types of signals; (a) the unsubstituted cyclopentadienyl ring of the ferrocene exhibits a sharp singlet around 4.19–4.25 ppm, (b) the mono substituted cyclopentadienyl ring of ferrocene exhibit triplet at of 4.50 ppm, (c) the olefinic proton appears as singlet in the region 7.54–8.15 ppm.

The ^{1}H NMR spectrum of the donor–acceptor compounds **10**–**14** shows five different types of signals; (a) the unsubstituted cyclopentadienyl ring of ferrocene exhibits a multiplet around 4.43–4.46 ppm, and triplet in the region of 4.87–4.89 ppm, (b) the mono substituted cyclopentadienyl ring exhibits triplet at 5.05 ppm, and multiplet at 5.47 ppm, (c) the olefinic proton appears as singlet in the region 7.67–8.20 ppm.

3. Photophysical properties

The electronic absorption spectra of the ferrocenyl substituted triphenylamine based donor–acceptor compounds **5**–**14** in dichloromethane solution are shown in Fig. 1, and the data are listed in Table 1. The UV–vis absorption spectrum of the compounds **6**–**9** show two types of bands. The first band in the region 349–367 nm corresponds to $\pi \rightarrow \pi^{*}$ transition, and the second band in the region 415–502 nm corresponds to intramolecular charge transfer (ICT).[11] Compound **7** shows intense ICT band (λ_{max} ~502 nm), which involves the transition from the ferrocenyl substituted triphenylamine donor to the acceptor 1,3-inadanone, whereas compound **9** shows moderate charge transfer from ferrocenyl substituted triphenylamine to tetralone around 415 nm (Fig. 1a). The strength of the ICT in compounds **6**–**9**, follows the order **7**>**6**>**8**>**9**.



(a) (b)

Fig. 1. Normalized electronic absorption spectra of the ferrocenyl substituted triphenylamine based donor–acceptor compounds **5**–**14** in CH_2Cl_2 (1.0×10^{-4} M). (a) Compounds **5**–**9**. (b) Compounds **10**–**14**.

The donor–acceptor compounds **10**–**14** show two types of bands, the first high energy absorption band around 469–502 nm corresponds to $\pi \rightarrow \pi^{*}$ transition, and the second low energy broad band around 630–700 nm corresponds to ICT (Fig. 1b). Compounds **5**–**9** show high intensity ICT band around 415–502 nm, whereas their TCNE derivatives **10**–**14**, show low-intensity ICT band around 630–700 nm.[12] This reveals that after addition of the TCNE, the primary acceptors (malononitrile, 1-indanone, 1,3-indanone, and tetralone) losses acceptor strength in the presence of TCNE (strong acceptor) groups, which is also evident from the computational studies and Figure 2 displays the colors of the donor–acceptor 10–14 in dichloromethane.

Table 1
Photophysical and electrochemical data of donor–acceptor compounds **5**–**14**

Compound	λ_{max} (nm)	ε[d] (M^{-1} cm^{-1})	E_{oxid} (V)	E_{red} (V)	Optical band gap[e] (eV)	Theoretical band gap[f] (eV)
5	359 —	27,600	0.05[a] 0.80[b]	—	3.01	3.42
6	349 459	8100	0.08[a] 0.71[b]	—	2.26	2.72
7	502	13,866	0.10[a] 0.81[b]	—	2.12	2.70
8	364 434	8700	0.07[a] 0.67[b]	—	2.54	2.80
9	367 415	10,000	0.06[a] 0.76[b]	—	2.61	2.88
10	485 —	56,666	0.41[a] 1.11[b]	1.43[c] 0.97[c]	2.21	2.76
11	469 —	11,066	0.42[a] 0.99[b]	1.39[c] 0.94[c]	2.25	2.74
12	488 —	15,733	0.39[a] 0.98[b]	1.41[c] 0.97[c]	2.11	2.73
13	499 —	48,500	0.43[a] 0.93[b]	1.37[c] 0.97[c]	2.11	2.67
14	502 —	7666	0.44[a] 0.89[b]	1.39[c] 0.97[c]	2.02	2.61
Ferrocene	—	—	0.00	—	—	—

[a] The oxidation value of ferrocene unit.
[b] The oxidation value of triphenylamine unit.
[c] The reduction values of TCNE group.
[d] Measured in dichloromethane solvent.
[e] Optical band gap estimated from the absorption edge.
[f] Theoretical values from DFT calculations.

4. Electrochemical properties

The electrochemical properties of the ferrocenyl substituted triphenylamine based donor–acceptor compounds **5**–**14** were studied by the cyclic voltammetric analysis. The electrochemical data of compounds **5**–**14** are listed in Table 1, and the representative cyclic voltammograms are shown in Fig. 3. The cyclic voltammogram of compounds **5**–**9** shows two oxidation waves; (a) the reversible wave in the region 0.05–0.1 V corresponding to the oxidation of ferrocene unit, (b) the quasi reversible oxidation wave in the region 0.67–0.81 V, which belongs to the triphenylamine unit.[13] Compounds **5**–**9** exhibit harder oxidation compared to free ferrocene, confirming strong electronic communication between ferrocene unit, and different acceptors. The trend in the oxidation potential of the ferrocenyl moiety in **5**–**9** follows the order **7**>**6**>**8**>**9**>**5**, which reveals that the increase in the strength of acceptor unit improves the donor–acceptor interaction.

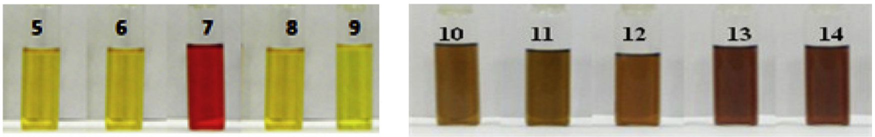
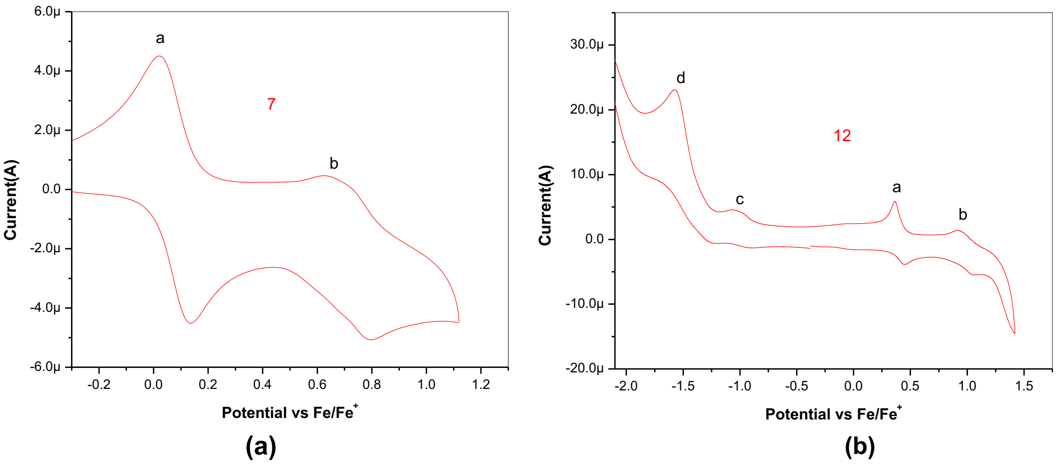


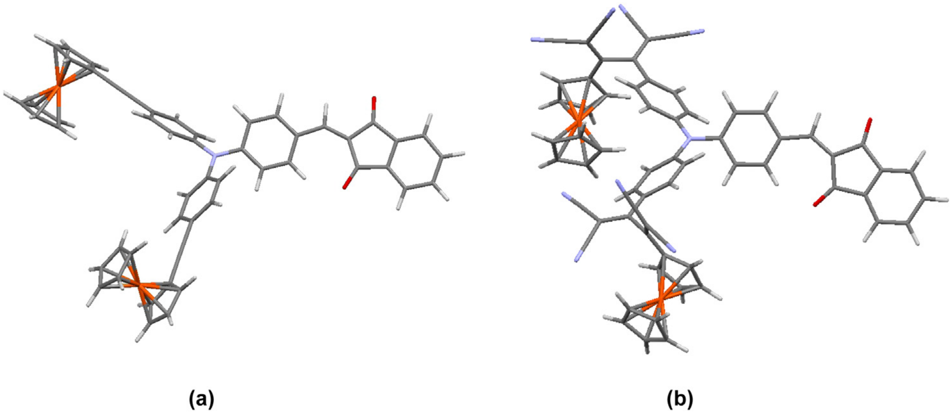
Fig. 2. The ferrocenyl substituted triphenylamine donor–acceptor compounds **5**–**14** show a prominent effect on their color pattern in dichloromethane solution 1.0×10^{-4} M.



(a) (b)

Fig. 3. Cyclic voltammograms of the ferrocenyl substituted triphenylamine based donor–acceptor (a) compound **7**, and (b) compound **12**, at 1.0×10^{-4} M concentration in 0.1M TBAPF$_6$ in dichloromethane recorded at a scan rate of 100 mV s^{-1}.

Compounds **10**–**14** exhibit harder oxidation potential compared to compounds **5**–**9** due to increase in the number of acceptors (TCNE). The cyclic voltammogram of donor–acceptor compounds **10**–**14** show two oxidation waves, and two reduction waves. The first oxidation wave in the region 0.39–0.44 V corresponds to the oxidation of ferrocene unit, and the second quasi reversible wave in the region 0.89–1.11 V, which belongs to triphenylamine unit. The two reduction waves, one is quasi reversible in the region of 0.94–0.97 V, and another one is reversible in the region of 1.37–1.43 belongs to the TCNE group.[14]



(a) (b)

Fig. 4. Geometry optimized structures of the ferrocenyl substituted triphenylamine based donor–acceptor compounds (a) **7**, and (b) **12**, with Gaussian 09 at the B3LYP/6-31G** level of theory.

5. Theoretical calculations

The structural and electronic properties of the ferrocenyl substituted triphenylamine based donor–acceptor compounds **5**–**14** were explored by means of theoretical calculations. The structures of **5**–**14** (see Supplementary data) were optimized using density functional theory (DFT) with Gaussian 09 at the B3LYP/6-31G** for C, H, N, O, and Lanl2DZ for Fe level.[15,16] The ferrocenyl groups were found to be planar with respected to the phenyl ring in donor–acceptor compounds **5**–**9**. On the other hand the incorporation of the TCNE group results in loss of planarity of ferrocenyl groups due to steric hindrance in compounds **10**–**14**. The optimized structures of compounds **7** and **12** are shown in Fig. 4.

The theoretical calculations show good agreement with the electronic properties. The contours of the HOMO, and LUMO of compounds **5**–**9** are shown in Fig. 5.

In compounds **5**–**9** the HOMO orbitals are localized on the ferrocene, and the triphenylamine units, whereas the LUMO orbitals are mainly concentrated on the acceptor units (malononitrile, 1-indanone, 1,3-indanone, tetralone). The band gap in compounds **5**–**9** follows the order **5 > 9 > 8 > 6 > 7**.

The contribution of the HOMO and LUMO orbitals in compounds **10**–**14** undergoes a drastic change, due to the incorporation of the 1,1,4,4-tetracyanobuta-1,3-diene (TCBD) unit. The LUMO orbitals

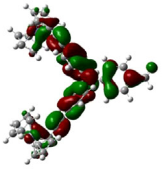
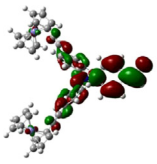
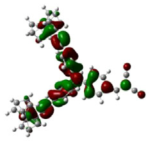
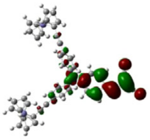
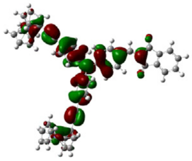
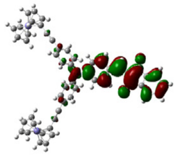
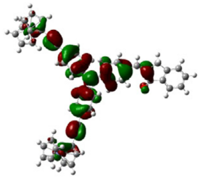
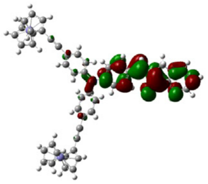
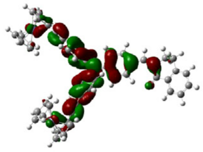
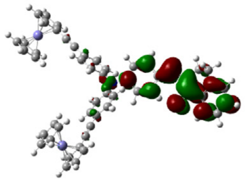
Compounds **5-9**	HOMO	LUMO	**Band-gap (eV)**
5	 -5.06	 -1.64	3.42
6	 -5.28	 -2.55	2.72
7	 -5.05	 -2.35	2.70
8	 -4.84	 -2.04	2.80
9	 -4.81	 -1.93	2.88

Fig. 5. Frontier molecular orbitals of the ferrocenyl substituted triphenylamine donor–acceptor compounds **5**–**9**.

are mainly concentrated on one of the TCBD unit, whereas the HOMO orbitals remain confined on one of the ferrocene unit in compounds **10** and **11** and on the triphenylamine unit in compounds **12**, **13**, and **14** (Fig. 6).

Compounds **10**–**14** show lower band gap values compared to the compounds **5**–**9**, which is attributed to the presence of strong electron withdrawing TCBD units (Fig. 7).

6. Conclusion

In summary a series of ferrocenyl substituted triphenylamine based donor–acceptor compounds were synthesized by the Pd-catalyzed Sonogashira cross-coupling, and Knoevenagel condensation reactions. The cycloaddition reaction of **5**–**9** with TCNE resulted new series of donor–acceptor compounds **10**–**14**. The electronic absorption, and cyclic voltammetric studies suggests substantial donor–acceptor interaction. The band gap in these donor–acceptor molecular system can be reduced by the incorporation of 1,1,4,4-tetracyanobuta-1,3-diene (TCBD) group. The detailed photonic applications of these materials are underway.

7. Experimental section

7.1. General experimental

^{1}H NMR (400 MHz), and ^{13}C NMR (100 MHz) spectra were recorded on 400 MHz. Chemical shifts in ^{1}H NMR, and ^{13}C NMR spectra were reported in parts per million (ppm) with TMS (0 ppm), and $CDCl_3$ (77.23 ppm) as standards. UV–visible absorption spectra of all compounds were recorded in DCM. Cyclic voltammograms (CVs) were recorded on electrochemical analyzer using Glassy carbon as working electrode, Pt wire as the counter electrode, and

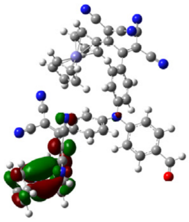
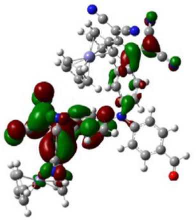
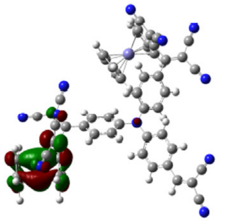
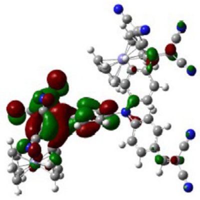
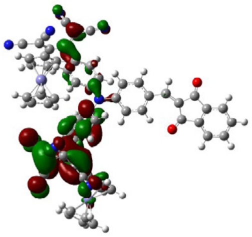
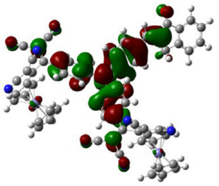
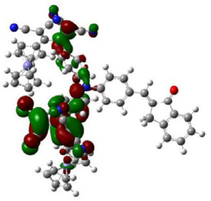
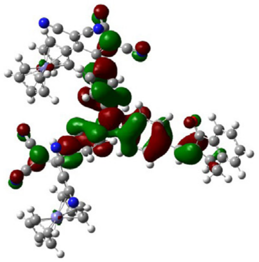
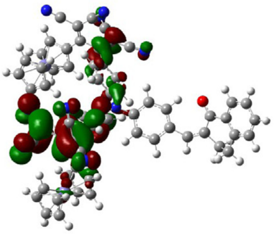
Compounds **10-14**	HOMO	LUMO	**Band -gap (eV)**
10	 -6.30	 -3.54	2.76
11	-  -6.41	 -3.67	2.74
12	 -6.21	 -3.48	2.73
13	 -6.14	 -3.47	2.67
14	 -6.03	 -3.41	2.61

Fig. 6. Frontier molecular orbitals of the ferrocenyl substituted triphenylamine donor–acceptor compounds **10**–**14**.

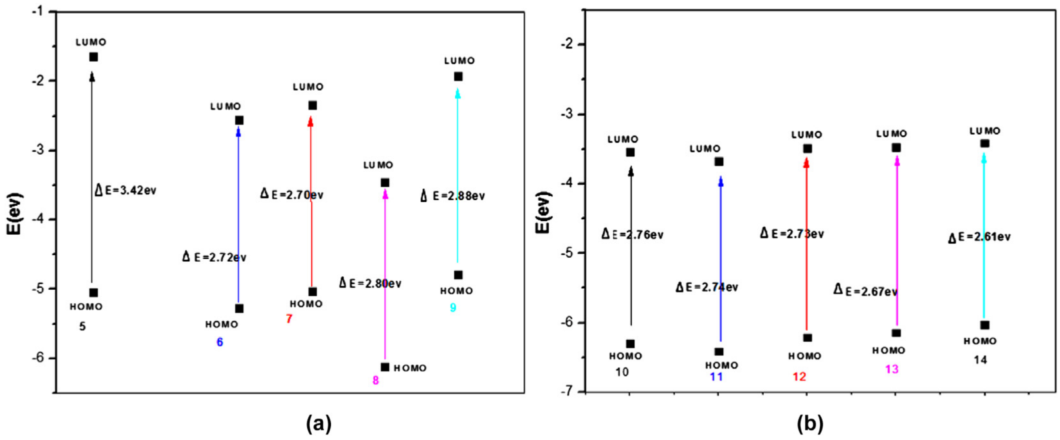


Fig. 7. Calculated HOMO and LUMO levels for: (a) the donor–acceptor compounds **5**–**9**; (b) the donor–acceptor compounds **10**–**14**.

saturated calomel electrode (SCE) as the reference electrode. The scan rate was 100 mV s^{-1} for CV. A solution of tetrabutylammoniumhexafluorophosphate ($TBAPF_6$) in CH_2Cl_2 (0.1 M) was employed as the supporting electrolyte. DCM was freshly distilled from CaH_2 prior to use. All potentials were experimentally referenced against the saturated calomel electrode couple but were then manipulated to be referenced against Fc/Fc^+ as recommended by IUPAC. Under our conditions, the Fc/Fc^+ couple exhibited $E°=0.38$ V versus SCE. HRMS was recorded on TOF-Q mass spectrometer. All reagents were obtained from commercial sources, and used as received unless otherwise stated.

7.2. General procedure for the preparation of compounds 2, 3, and 5–14

Compound **2** was synthesized by the Vilsmeier–Haack formylation reaction of triphenylamine **1**.[9] Compound **3** synthesized from compound **2** according to the literature procedure.[10]

7.2.1. Synthesis of compound ***5***. 4-[Bis-(4-ethynyl ferrocenyl-phenyl)-amino]-benzaldehyde (**5**). A mixture of 4-(bis(4-iodophenyl)amino)-benzaldehyde (2 g, 3.80 mmol), and ethynyl ferrocene (4 g, 9.52 mmol) was dissolved in dry THF (30 ml), added triethylamine (15 ml), $Pd(PPh_3)_4$ (0.100 g, 0.08 mmol), stirred for 16 h at 60 °C under argon atmosphere, after completion of the reaction, the reaction mixture was concentrated under reduced pressure, the crude compound was purified by flash column chromatography (40% hexane/CH_2Cl_2) to give title compound **5** (1.712 g, 65%) as a orange solid; mp >300.0 °C; R_f (40% hexane/CH_2Cl_2) 0.45; δ_H (400 MHz, $CDCl_3$) 9.86 (s, 1H), 7.74–7.72 (d, 2H, J=8 Hz), 7.45–743 (d, 4, J=8 Hz), 7.12–7.09 (t, 6H), 4.51–4.50 (t, 4H, J=4 Hz), 4.25 (t, 12H); δ_C (100.0 MHz, $CDCl_3$) 191.0, 152.4, 145.3, 132.8, 131.3, 130.2, 125.5, 121.1, 120.4, 88.9, 85.2, 71.5, 70.1, 69.0, 65.4; HRMS: M^+ found 689.1104, $C_{43}H_{31}Fe_2NO$ requires 689.1101.

7.3. General procedure for the preparation of compounds 6 and 7

The mixture of compound **5** (0.1 g, 0.14 mmol) and corresponding active methylene derivative (malononitrile, indan-1,3-dione) (0.023 g, 0.95 mmol) was dissolved in dry DCM (5 ml), added ammonium acetate (0.073g, 0.94 mmol) stirred for 3 h at 65 °C in microwave, after completion of the reaction, reaction mixture was concentrated under reduced pressure, the crude compound was purified by column chromatography (80% hexane/CH_2Cl_2) to give title compounds **6** and **7**.

*7.3.1. 2-{4-[Bis-(4-ethynyl-phenyl)-amino]-benzylidene}-malononitrile (**6**).* Orange solid (0.091 g, 85%); mp >345.0 °C; R_f (50% hexane/CH_2Cl_2) 0.23; δ_H (400 MHz $CDCl_3$) 7.78–7.76 (d, 2H, J=8 Hz), 7.55 (s, 1H), 7.48–7.46 (d, 4H, J=8 Hz), 7.13–7.11 (d, 4H, J=8 Hz), 7.06–7.04 (d, 2H, J=8 Hz), 4.51 (t, 4H, J=4 Hz), 4.27–4.25 (d, 13H, J=4 Hz); δ_C (100.0 MHz, $CDCl_3$) 157.8, 152.5, 144.2, 132.9, 132.9, 126.0, 123.9, 121.5, 120.0, 113.8, 89.5, 85.0, 71.5, 70.0, 69.0, 64.9; HRMS: M^+ found 737.1216. $C_{46}H_{31}Fe_2N_3$ requires 737.1213.

*7.3.2. 2-{4-[Bis-(4-ethynyl-phenyl)-amino]-benzylidene}-indan-1,3-dione (**7**).* Red solid (0.095 g, 80%); mp >360.0 °C; R_f (85% hexane/CH_2Cl_2) 0.20; δ_H (400 MHz $CDCl_3$) 7.78–7.76 (d, 2H, J=8 Hz), 7.55 (s, 1H), 7.48–7.46 (d, 6H, J=8 Hz), 7.12–7.10 (d, 6H, J=8 Hz), 7.06–7.04 (d, 2H, J=8 Hz), 4.51–4.50 (t, 4H, J=4 Hz), 4.26–4.25 (d, 13H, J=4 Hz); δ_C (100.0 MHz, $CDCl_3$) 157.8, 152.5, 144.2, 132.9, 126.0, 123.9, 121.5, 120.0, 114.9, 113.5, 89.5, 85.0, 71.5, 70.0, 69.0, 64.9; HRMS: M^+ found 817.1361. $C_{52}H_{35}Fe_2NO_2$ requires 817.1364.

7.4. General procedure for the preparation of compounds 8 and 9

The mixture of compound **5** (0.1 g, 0.14 mmol), and active methylene derivatives (1-indanone, 1-tetralone) (0.072, 0.54 mmol) was dissolved in dry in ethanol and THF (30:10) as solvent, added 10% NaOH or LiOH solution (1 ml), stirred for 16 h at 85 °C, after completion of the reaction, reaction mixture was allowed to cool to room temperature, then quenched with cold water (0.5 ml), orange solid gets precipitated, filtered dried under vacuum, crystallized with CH_2Cl_2/ethanol (1:3) to give title compounds **8** and **9**.

*7.4.1. 2-{4-[Bis-(4-ethynyl-phenyl)-amino]-benzylidene}-indan-1-one (**8**).* Orange solid (0.088 g, 75%); mp >360.0 °C; R_f (50% hexane/CH_2Cl_2) 0.23; δ_H (400 MHz $CDCl_3$) 7.93–7.91 (d, 1H)7.64 (s, 1H), 7.61–7.55 (q, 4H), 7.43–7.41 (d, 5H, J=8 Hz), 7.15–7.13 (d, 3H, J=8 Hz), 7.10–7.08 (d, 4H, J=8 Hz), 4.51–4.50 (t, 4H, J=4 Hz), 4.25–4.24 (d, 12H, J=4 Hz), 4.03 (s, 2H); δ_C (100.0 MHz, $CDCl_3$) 194.3, 149.4, 145.8, 138.3, 132.9, 132.6, 132.1, 127.7, 126.1, 124.7, 123.0, 119.4, 88.4, 85.4, 71.3, 70.0, 68.8, 65.3, 32.5; HRMS: M^+ found 803.1567. $C_{52}H_{37}Fe_2NO$ requires 803.1571.

*7.4.2. 2-{4-[Bis-(4-ethynyl-phenyl)-amino]-benzylidene}-1-tetralone (**9**).* Orange solid (0.083 g, yield 70%); mp >360.0 °C; R_f (50% hexane/CH_2Cl_2) 0.22; δ_H (400 MHz $CDCl_3$) 8.13–8.11 (dd, 1H, J=8 Hz), 7.84 (s, 1H), 7.51–7.47 (ddd, 2H, J=8 Hz), 7.41–7.38 (m, 7H), 7.13–7.07 (dd, 6H, J=8 Hz), 4.50–4.49 (t, 4H, J=4 Hz), 4.30–4.24 (t, 12H, J=4 Hz), 3.18–3.16 (t, 2H, J=4 Hz), 2.99–2.96 (t, 2H, J=4 Hz); δ_C

(100.0 MHz, $CDCl_3$) 187.7, 148.0, 146.1, 143.1, 136.4, 134.0, 132.6, 131.5, 128.1, 124.3, 123.2, 118.9, 88.2, 85.5, 71.4, 70.0, 68.8, 65.4, 28.8, 27.3; HRMS: M^+ found 817.1727. $C_{53}H_{39}Fe_2NO$ requires 817.1727 $[M^+]$.

7.5. General procedure for the preparation of compounds 10–14

To a solution of ferrocenyl substituted triphenylamine based donor–acceptor compounds (**10**–**14**) (0.05 g, 0.72 mmol) in CH_2Cl_2 (5 ml), TCNE (0.022 g, 1.77 mmol) was added, and the mixture was stirred at 75 °C for 3 h in microwave, after completion of the reaction, the reaction mixture was concentrated under reduced pressure, the crude compound was purified by column chromatography (5% CH_2Cl_2/EtOAC) to give title compounds (**10**–**14**).

*7.5.1. 3-(4-{Bis-[4-(3,3-dicyano-1-dicyanomethylene-2-ferrocenyl-allyl)-phenyl]-amino}-benzaldehyde (**10**).* Light wine solid (0.049 g, 72%); mp >380.0 °C; R_f (5% CH_2Cl_2/EtOAC) 0.50; δ_H (400 MHz $CDCl_3$) 9.98 (s, 1H), 7.89–7.88 (d, 2H, J=4 Hz), 7.58–7.56 (d, 5H, J=8 Hz), 7.14–7.13 (d, 5H, J=4 Hz), 5.54 (s, 2H), 5.04 (s, 2H), 4.89 (s, 2H), 4.46 (s, 12H); δ_C (100.0 MHz, $CDCl_3$) 208.9, 190.5, 177.5, 164.2, 142.4, 136.3, 131.8, 130.9, 126.2, 124.0, 118.1, 113.5, 90.9, 72.8, 72.6, 72.5, 72.3, 71.0; HRMS: M^{+n}Na found 968.1248. $C_{55}H_{31}Fe_2N_9O$ requires 968.1245.

*7.5.2. 3-(4-{Bis-[4-(3,3-dicyano-1-dicyanomethylene-2-ferrocenyl-allyl)-phenyl]-amino}-phenyl)-2-malononitrile (**11**).* Light wine solid red solid (0.042 g, 60%); mp >380.0 °C; R_f (5% CH_2Cl_2/EtOAC) 0.32; δ_H (400 MHz $CDCl_3$) 7.90–7.89 (d, 2H, J=4, Hz), 7.68 (s, 1H), 7.59–7.57 (d, 4H, J=8 Hz), 7.21–7.15 (m, 6H, J=4 Hz), 5.48 (s, 2H), 5.05 (s, 2H), 4.90 (s, 2H), 4.47 (s, 11H); δ_C (100.0 MHz, $CDCl_3$) 164.2, 132.9, 131.0, 127.2, 125.3, 124.5, 112.0, 111.8, 84.4, 82.0, 76.1, 72.9, 72.7, 71.2. HRMS: M^{+n}Na found 1016.1356. $C_{58}H_{31}Fe_2N_{11}$ requires 1016.1358.

*7.5.3. .3-(4-{Bis-[4-(3,3-dicyano-1-dicyanomethylene-2-ferrocenyl-allyl)-phenyl]-amino}-2-(indane-1,3-dione) (**12**).* Light wine solid (0.040 g, 61%); mp >380.0 °C; R_f (5% CH_2Cl_2/EtOAC) 0.25; δ_H (400 MHz $CDCl_3$) 8.50–8.48 (d, 2H, J=8 Hz), 8.01 (s, 2H), 7.83 (s, 3H), 7.59–7.57 (d, 4H, J=8 Hz), 7.19–7.17 (d, 5H, J=8 Hz), 5.45 (s, 2H), 5.05 (s, 2H), 4.90 (s, 2H), 4.54–4.47 (d, 9H); δ_C (100.0 MHz, $CDCl_3$) 190.0, 164.2, 150.2, 148.1, 140.1, 136.3, 136.0, 130.9, 127.0, 125.8, 124.2, 123.4, 113.5, 112.9, 112.2, 112.0, 83.1, 76.0, 75.0, 72.8, 72.6, 71.2; HRMS: M^{+n}Na found 1096.1504. $C_{64}H_{35}Fe_2N_9O_2$ requires 1096.1508.

*7.5.4. 3-(4-{Bis-[4-(3,3-dicyano-1-dicyanomethylene-2-ferrocenyl-allyl)-phenyl]-amino}-phenyl)-2-(indane-1-one) (**13**).* Light wine solid (0.045 g, 69%); mp >380.0 °C; R_f (5% CH_2Cl_2/EtOAC) 0.25; δ_H (400 MHz $CDCl_3$) 7.93–7.92 (d, 1H, J=8 Hz), 7.71–7.69 (d, 2H, J=8 Hz), 7.63 (s, 2H), 7.57–7.55 (d, 5H, J=4 Hz), 7.47–7.43 (t, 2H, J=8 Hz), 7.21–7.19 (d, 2H, J=8 Hz), 7.16–7.14 (d, 3H, J=8 Hz), 5.44 (s, 2H), 5.04 (s, 2H), 4.89 (s, 2H), 4.54–4.46 (m, 12H), 4.04 (s, 2H); δ_C (100.0 MHz, $CDCl_3$) 181.1, 164.2, 155.7, 150.5, 135.6, 134.9, 132.6, 130.9, 127.0, 126.2, 123.4, 113.5, 112.9, 112.1, 76.0, 75.0, 72.8, 72.6, 71.2; HRMS: M^{+n}Na found 1082.1716. $C_{64}H_{37}Fe_2N_9O$ requires 1082.1716.

*7.5.5. 3-(4-{Bis-[4-(3,3-dicyano-1-dicyanomethylene-2-ferrocenyl-allyl)-phenyl]-amino}-phenyl)-2-(1-tetralone) (**14**).* Light wine solid (0.041 g, 63%); mp >380.0 °C; R_f (5% CH_2Cl_2/EtOAC) 0.24; δ_H (400 MHz $CDCl_3$) 8.14–8.12 (d, 1H, J=8 Hz), 7.81 (s, 1H), 7.58–7.51 (m, 4H, J=4 Hz), 7.49–7.47 (d, 3H, J=4 Hz), 7.40–7.36 (t, 2H, J=8 Hz), 7.17–7.13 (t, 6H, J=8 Hz), 5.44–5.43 (t, 2H, J=4 Hz), 5.04–5.03 (t, 2H, J=4 Hz), 4.89–4.87 (t, 2H, J=4 Hz), 4.55–4.53 (t, 2H, J=4 Hz), 4.46–4.44 (d, 10H), 3.15–3.12 (t, 2H), 3.00–2.97 (t, 2H); δ_C (100.0 MHz, $CDCl_3$) 187.5, 172.9, 164.1, 150.6, 143.3, 143.1, 136.4, 134.8, 133.5, 132.1, 130.9, 128.3, 127.0, 123.1, 113.5, 112.9, 112.4, 112.1, 82.8, 78.9, 75.1, 75.0, 72.8, 72.6, 71.2, 69.7, 28.8, 27.3; HRMS: M^{+n}Na, found 1096.1872. $C_{65}H_{39}Fe_2N_9O$ requires 1096.1872.

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Supplementary data

The optimized structures of compounds **5**–**14** with dihedral angles, cyclic voltammograms of compounds **5**–**14**, ^{1}H NMR, ^{13}C NMR spectra, mass spectroscopy data, UV–vis graphs, DFT calculations of compounds **5**–**14** are provided. Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2014.03.096.

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