

View Article Online View Journal

Journal of Materials Chemistry C

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: S. Kaur, N. Van Steerteghem, P. Kaur, K. Clays and K. Singh, *J. Mater. Chem. C*, 2016, DOI: 10.1039/C6TC03350D.



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about *Accepted Manuscripts* in the **Information for Authors**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the <u>Ethical guidelines</u> still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.



www.rsc.org/materialsC

Journal Name



Received 00th January 20xx, Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Synthesis, characterization and second-order nonlinear optical behaviour of ferrocene-diketopyrrolopyrrole dyads. Effect of alkene vs alkyne linkers

Sarbjeet Kaur,^a Nick Van Steerteghem,^b Paramjit Kaur,^{*,a} Koen Clays^b and Kamaljit Singh^{*,a}

New, thermally stable dipolar ferrocene-diketopyrrolopyrrole (Fc-DPP) dyads with alkene as linker exhibited structure dependent first hyperpolarizabilities, β_{HRS} recorded by femtosecond HRS technique using femtosecond (120 fs) pulsed laser light system at 900 nm at ambient temperature. On the basis of linear optical, electrochemical and TD-DFT studies, a good structure-polarization relationship has been established to account for the observed trends in first hyperpolarizabilities. The dyads exhibited fluctuating but matching solvatochromism. Nonlinear optical properties are modulated both by the strength of acceptor as well as the length and nature of the π -conjugation bridge. β_{HRS} of the dyads were compared with structurally related dyads in which DPP core and the Fc donor are linked via alkyne bridge. It is interesting to observe that the replacement of alkyne link with alkene in these D- π -A chromophores does not necessarily furnish enhanced β_{HRS} .

Introduction

The large second-order optical nonlinearity is often associated with dipolar polarization¹⁻⁵ of the non-centrosymmetric^{1,6-9} materials with intramolecular charge transfer (ICT) from donor (D) to acceptor (A), linked through efficient π -conjugated bridge. Such D- π -A type molecular systems have been investigated for their use in electrooptics and data storage devices, organic light emitting diodes (OLEDs), organic photovoltaics (OPVs), dye sensitized solar cells (DSSCs), nonlinear optical (NLO) switches etc.¹⁰⁻¹⁵ For the last few decades, the design and synthesis of organic and organometallic materials for such applications has fuelled interest of various researchers across the world.¹⁶⁻²⁶ Compared to inorganic materials (quartz, potassium dihydrogen phosphate, lithium niobate, etc.), the organic and organometallic materials offer several advantages such as structural flexibility in terms of modulation of strength of donor/acceptor, length of π -conjugation bridge and hence are easily tuneable for extracting attractive optical non-linearity. Organometallic materials are attractive as the introduction of redox active metal centre²⁷⁻³⁶ allows oxidation state guided switching of NLO behaviour of D- π -A dyads. Ferrocene (Fc) has been extensively used as redox-active moiety³⁷⁻³⁹. Also, the Fc dyads are characterized by low oxidation potential and upon facile charge transfer (CT) to an acceptor yield stable $\alpha\text{-}$ ferrocenyl carbocations and the NLO behaviour of a number of chromophores have been studied^{38,40-41} On the basis of UVvisible absorption, electrochemical, theoretical studies as well as hyper Rayleigh scattering (HRS) experiments, very recently, we have demonstrated the effect of donor (Fc), acceptor (diketopyrrolopyrrole,⁴² DPP and α -cyanostilbenes⁴³) and π conjugation bridge on the second-order nonlinear optical polarizability or first hyperpolarizability (β_{HRS}). In one of these reports, second-order nonlinear behaviour of D- π -A and D- π -A- π -D dipolar chromophores having mono- or disubstituted Fc (D) linked to DPP (A) motif via alkynyl bridge has been revealed.42 In these chromophores, DPP acts as strong acceptor due to the presence of two strong electron withdrawing amide groups.⁴⁴⁻⁴⁶ The inbuilt structural planarity coupled with low lying LUMOs (lowest unoccupied molecular orbitals), high photochemical as well as thermal stability, of DPP makes it attractive motif to be used in electrooptic devices.47-61

In accordance with the literature precedence, alkenes (C=C) possess better conjugating ability than alkynes (C=C)^{37,62-66} and hence more charge transfer is expected in the former leading to comparatively higher first hyperpolarizability (β). In order to test this hypothesis and to further extend the scope and limitations of such NLO active chromophores, in this paper we have synthesized D- π -A- π -A' type dipolar chromophores using Fc and DPP linked via alkene bridge (Figure 1). Their first hyperpolarizability (β_{HRS}) was recorded in chloroform solutions at 900 nm using femtosecond (120 fs) pulsed laser light. To the best of our knowledge, Fc-DPP dyads with alkene linker have not been reported yet.

^{a.} Department of Chemistry, UGC Centre of Advanced Study-II, Guru Nanak Dev University, Amritsar-143005, India. Email: <u>kamaliit.chem@andu.ac.in</u>

^{b.} Department of Chemistry, University of Leuven, Celestijnenlaan 200D, B-3001 Leuven, Belgium. E-mail: <u>Koen.Clays@fys.kuleuven.be</u>

Electronic Supplementary Information (ESI) available: [1 H NMR and 13 C NMR, UV-visible/fluorescence/CV and TGA data, Computational studies]. See DOI: 10.1039/x0xx00000x

DOI: 10.1039/C6TC03350D Journal Name



The dyads were characterized using ¹H and ¹³C NMR, HRMS, UV-visible absorption and FTIR spectroscopy. A good correlation between the experimental spectroscopic properties of the dyads with the properties computed by employing ab initio density functional theory (DFT) calculations and time-dependent DFT (TD-DFT) calculations (Gaussian 09) has been achieved. In order to simplify the UV-visible absorption spectra, spectral resolution has been achieved by band fitting. Moreover, the structure-polarization (dipole moment) relationship has been analyzed and the effect of the molecular design on the observed linear, electrochemical and NLO properties has also been discussed. To deduce the figure of merit, we have drawn comparison of the current results with those of Fc-DPP chromophores having an alkyne linker, previously reported by us⁴² as well as the molecules reported in literature (Table S1, ESI⁺).

EXPERIMENTAL SECTION

Materials and reagents

All liquid reagents were dried/purified by using the recommended drying agents and/or distilled over 4 Å molecular sieves. Toluene was dried using sodium metal/benzophenone. Triethylamine was distilled and stored over KOH under nitrogen. Acetyl ferrocene 1,67 vinylferrocene $\mathbf{3}$,⁶⁸ DPP precursors $\mathbf{4}$ and $\mathbf{6}^{42}$ were prepared following the reported procedures. Ferrocene, palladium (II) acetate $(Pd(OAc)_2),$ triphenylphosphine, tetra-n-butylammonium bromide and sodium borohydride (NaBH₄) were purchased from Spectrochem and used as received. Tetrakis(triphenylphosphine)palladium (0) was purchased from SIGMA ALDRICH and used as such.

Instrumentation

UV-visible studies were carried out using UV-1800 SHIMADZU UV-visible spectrophotometer using quartz cuvettes (path length = 1 cm). Spectroelectrochemical studies were performed using Spectroelectrophotometer K-MAC SV2100-BF-0121. Fluorescence studies were carried out using Perkin Elmer LS 55 Fluorescence Spectrometer. IR spectrum was recorded on Perkin-Elmer FTIR-C92035 Fourier-transform spectrophotometer in range 400–4000 cm⁻¹ as KBr pellets.

Electrochemical measurements were made using CHI660D electrochemical workstation using three electrodes- platinum as working as well as counter electrode and Ag/AgCl as reference electrode. The experiments were carried at 1 x 10⁻⁴ M solution of the compound in dichloromethane (DCM) using 2×10^{-2} M tetrabutylammoniumhexafluorophosphate (TBAPF₆) as supporting electrolyte. The solutions were purged with nitrogen gas for 10 min and the working electrode as well as the reference electrode was cleaned after each recording. The experiments were carried out at scan rate of 100 mVs⁻¹. Thermogravimetric analysis (TGA) was performed on TGA/DSC 1 STAR SYSTEM FROM METTLER TOLEDO in the temperature range of 0-800 °C at the heating rate of 10 °C min⁻¹ under nitrogen atmosphere. For column chromatography, silica gel (60-120 mesh) was employed and the columns were eluted with ethyl acetate/hexane. All reported yields are isolated yields. Melting points were recorded in open capillaries and are uncorrected. ¹H NMR and ¹³C NMR spectra were recorded on Bruker Biospin Avance III HD at 500 MHz, in CDCl₃ containing TMS as internal standard. Data is presented as follows: chemical shift in ppm (δ), integration, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, br = broad) and coupling constant J (Hz). Mass spectrum (HRMS) was recorded on Bruker HRMS MICROTOF II spectrometer. Femtosecond HRS measurements⁶⁹⁻⁷⁴ were carried out in dilute solutions $(10^{-4} \text{ M}, \text{ filtered through } 0.45 \,\mu\text{m}$ Millipore filter paper) using a high-repetition (80 MHz), femtosecond (\approx 120 fs) pulsed Insight[®] DS+ laser system, able to produce peak powers up to 1.2 W over the range 680-1300 nm. Depending upon the wavelength, the actual power used in the experiments was in the range 500-600 W. In this set up, the collection optics are coupled to a spectrograph (model Bruker 500is/sm), together with an EMCCD camera (Andor Solis model iXon Ultra 897). The correction for multi-photon induced fluorescence was done by fitting the obtained spectra and only extracting the HRS peak (FWHM 7-8 nm). The higher accuracy of this set up enables us to use the solvent (CHCl₃) as internal reference with $\beta_{\rm HRS}$ of 0.2107 x 10⁻³⁰ esu, 0.1975 x 10⁻³⁰ esu and 0.1964 x 10⁻³⁰ esu recorded at 900 nm, 1240 nm and 1300 nm, respectively.

Computational details

To get a deeper insight into the effect of varying donor, acceptor and the nature of π -conjugation on the dipole moment, second-order nonlinear optical polarizability (β) and other related properties, theoretical calculations were carried out by using the Gaussian 09 suite of programs.⁷⁵ Optimization of molecular geometries of all the dyads and related calculations were performed by DFT method using B3LYP functional group and 6-31G as the basis set. The first 15-20 excited states were calculated by using TD-DFT calculations in gas phase as well in dichloromethane as solvent using CPCM model. The molecular orbital contours were plotted using Gauss view 5.0.9.

Synthesis of dyads and intermediates

Synthesis of 1-ferrocenylethanol 2

Published on 27 September 2016. Downloaded by UNIVERSITY OF NEW ORLEANS on 29/09/2016 15:15:13.

Journal Name

A solution of acetylferrocene, 1 (5g, 21.93 mmol) in methanol (70 ml) was added drop wise using dropping funnel to the 100 ml round-bottom flask containing suspension of NaBH₄ (2.5g, 65.79 mmol) in 40 ml water. The reaction mixture was allowed to stir 12 h at ambient temperature to obtain orange precipitates of 2. The solid was filtered, washed thoroughly with water and dried under vacuum. The solid was recrystallized from hexane to obtain analytically orange solid 2 (83 %). Mp 60-62 $^{\circ}C$ (Hexane) IR (KBr): ν_{max} 1022, 1068, 1105, 1237, 1306, 1410, 2931, 2974, 3089 and 3211 $\rm cm^{-1}$ $^{1}\rm H$ (500 MHz, CDCl₃, 25 °C): δ (ppm) 1.44 (d, J = 10 Hz, 3H, -CH₃), 1.83 (d, J = 5 Hz, 1H, -OH), 4.16-4.23 (m, 9H, Fc) and 4.52-4.57 (m, 1H, -CH). ¹³C NMR (125 MHz, CDCl₃, 25 °C): δ (ppm) 23.89, 65.76, 66.31, 68.08 and 68.44. HRMS: m/z calculated for C₁₂H₁₄OFe: 230.0389. Found: 230.0419 (M⁺).

Synthesis of vinylferrocene 3

1-Ferrocenylethanol 2 (4 g, 17.4 mmol) was mixed with activated neutral alumina (1:3 ratio) in mortar. The resulting mixture was covered with layer of neutral alumina and heated at 90-100 °C under vacuum. The orange crystals of vinylferrocene sublime and were collected to obtain analytically pure vinyl ferrocene, 3 (50 %). Mp 55-57 °C. IR (KBr): ν_{max} 1026, 1045, 1102, 1239, 1408, 1631, 2924, 3006 and 3080 cm⁻¹. ¹H (500 MHz, CDCl₃, 25 °C): δ (ppm) 4.10 (s, 5H, Fc), 4.20 (s, 2H, Fc), 4.35 (s, 2H, Fc), 5.02 (d, J = 10 Hz, 1H, CH=CH_{trans}H_{cis}), 5.33 (d, J = 20 Hz, 1H, CH=CH_{trans}H_{cis}) and 6.42-6.47 (m, 1H, C<u>H</u>=CH_{trans}H_{cis}). ¹³C NMR (125 MHz, CDCl₃, 25 °C): δ (ppm) 66.66, 68.64, 69.20, 111.03 and 134.66. HRMS: m/zcalculated for $C_{12}H_{12}Fe: 212.0283$. Found: 212.0313 (M^+).

Synthesis of 4-(5-(4-(5-bromofuran-2-yl)-2,5-didecyl-3,6-dioxo-2,3,5,6-tetrahydropyrrolo[3,4-c]pyrrol-1-yl)furan-2yl)benzaldehyde 7

A solution of 4 (0.100 g, 0.1 mmol), p-formylphenylboronic acid (0.018g, 0.12 mmol) and tetrabutylamonium bromide (2.5 mg, 0.0065 mmol) in toluene (dry, 30 ml) was taken in 100 ml two-necked round bottom flask equipped with reflux condenser. The solution was degassed and purged with N₂ for 15 min. After that, Pd(0) (7.0 mg, 0.0077 mmol) was added and the reaction mixture was again degassed and purged with N₂. To the resulting solution, was added 2 ml of 2M Na₂CO₃ solution via cannula under inert atmosphere and the reaction mixture was refluxed for 5-6 h. After completion (TLC), toluene was evaporated under vacuum and the reaction mixture was extracted with chloroform (3 x 25 ml). The extract was washed with water (2 x 20 ml), dried over anhydrous sodium sulfate and evaporated under reduced pressure to obtain crude 7, which was purified by column chromatography using 5:95 (EtOAc/hexane) as eluents to obtain dark red solid 7 (60%). Mp 138-140 $^{\rm o}C$ IR (KBr): v_{max} 1211, 1390, 1467, 1589, 1604, 1665, 1705, 2852, 2923, 2952, 3104 and 3132 cm⁻¹ ¹H (500 MHz, CDCl₃, 25 °C): δ (ppm) 0.87 (t, J = 7.5 Hz, 6H, -CH₃), 1.25-1.43 (m, 28H, -CH₂), 1.58-1.81 (m, 4H, -CH₂), 4.07 (t, J = 7.5 Hz, 2H, -CH₂), 4.20 (t, J = 7.5 Hz, 2H, -CH₂), 6.63 (d, J = 5 Hz, 1H, furanyl C4' -CH), 7.12 (d, J = 5 Hz, 1H, furanyl C3' -CH), 7.87 (d, J = 5 Hz, 2H, phenyl-CH), 7.95 (d, J = 5 Hz, 2H, phenyl-CH), 8.28 (d, J = 5

Hz, 1H, furanyl C4-CH), 8.39 (d, J = 5 Hz, 1H, furanyl C3-CH) and 10.03 (s, 1H, -CHO). ¹³C NMR (125 MHz, CDCl₃, 25 $^{\circ}$ C): δ (ppm) 14.11, 22.70, 26.90, 27.14, 29.31, 29.37, 29.54, 29.60, 29.71, 30.37, 31.26, 31.94, 38.18, 42.57, 42.78, 106.68, 107.60, 111.73, 115.57, 122.26, 124.63, 126.55, 130.49, 132.49, 132.74, 134.44, 135.97, 145.15, 146.19, 155.21, 160.61 and 191.07. HRMS: *m/z* calculated for C₄₁H₅₁BrN₂O₅: 731.3054 and 733.3042 (M⁺+2). Found: 731.3085 (M⁺) and 733.3072 (M⁺+2).

DOI: 10.1039/C6TC03350D

ARTICLE

General procedure for synthesis of 5a-c For the synthesis of 5a, anhydrous nitrogen gas was filled in a septum capped twoneck round bottom flask containing 4 (0.1 g, 0.14 mmol), 3 (0.045 g, 0.21 mmol), palladium (II) acetate (4.7 mg, 0.021 mmol) and triphenylphosphine (7.3 mg, 0.028 mmol). Under the inert atmosphere, was added toluene (dry, 30 ml) and triethylamine (0.142 g, 1.4 mmol) and the reaction mixture was allowed to reflux for 6 h. After completion (TLC), toluene was evaporated under vacuum and the reaction mixture was extracted with chloroform (3 x 25 ml). The extract was washed with water (2 x 20 ml), dried over anhydrous sodium sulfate and evaporated under reduced pressure to obtain crude 5a, which was purified by column chromatography using 3:97 (EtOAc/hexane) as eluents to obtain dark blue solid 5a (33%).

Following the above procedure and using 6 (0.1 g, 0.2 mmol), 3 (0.128 g, 0.6 mmol), palladium (II) acetate (4.0 mg, 0.02 mmol), triphenylphosphine (0.01 g, 0.04 mmol), triethylamine (0.202 g, 1.0 mmol) in toluene (dry, 10 ml) under inert atmosphere yielded 5b (30 %). Similarly, 5c was obtained in 35 % yield using 7 (0.19 g, 0.26 mmol), 3 (0.166 g, 0.78 mmol), palladium (11) acetate (6.4 mg, 0.028 mmol), triphenylphosphine (0.016 g, 0.052 mmol), triethylamine (0.263 g, 2.6 mmol) in toluene (dry, 10 ml) under inert atmosphere.

(E)-3-(5-bromofuran-2-yl)-2,5-didecyl-6-(5-

vinylferrocenyl)furan-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)dione 5a Dark blue solid (33 %). Mp 110-115 °C (Methanol). IR (KBr): v_{max} 1016, 1104, 1261, 1384, 1585, 1657, 2852, 2922, 2957 and 3031 cm⁻¹, ¹H (500 MHz, CDCl₃, 25 $^{\circ}$ C): δ (ppm) 0.87 (t, J = 5 Hz, 6H, -CH₃), 1.25-1.54 (m, 28H, -CH₂), 1.68-1.83 (m, 4H, -CH₂), 4.08 (t, J = 7.5 Hz, 2H, -CH₂), 4.17-4.21 (m, 7H, Fc and -CH₂), 4.40 (s, 2H, Fc), 4.48 (s, 2H, Fc), 6.53 (br, t, J = 10 Hz, 2H, furanyl C4'-CH and vinyl-CH), 6.62 (d, J = 5 Hz, 1H, furanyl C3'-CH), 6.96 (d, J = 15 Hz, 1H, vinyl-CH), 8.21 (d, J = 5 Hz, 1H, furanyl C4-CH) and 8.39 (d, J = 5 Hz, 1H, furanyl C3-CH). ¹³C NMR (125 MHz, CDCl₃, 25 $^{\circ}$ C): δ (ppm) 13.11, 21.65,21.67, 25.87, 26.33, 28.29, 28.52, 28.59, 28.68, 28.74, 29.23, 29.29, 30.86, 30.88, 41.45, 41.83, 66.33, 68.51, 69.14, 105.01, 105.92, 109.96, 111.77, 114.36, 120.10, 122.83, 124.67, 129.85, 130.02, 132.36, 142.04, 145.45, 156.14, 159.36 and 159.94. HRMS: m/z calculated for C46H57BrFeN2O4: 836.2848 and 838.2837. Found: 836.2880 (M⁺) and 838.2870 (M⁺+2).

(E)-5-(2,5-didecyl-3,6-dioxo-4-(5-vinylferrocenyl)furan-2-yl)-2,3,5,6-tetrahydropyrrolo[3,4-c]pyrrol-1-yl)furan-2-

carbaldehyde 5b Dark blue solid (30 %). Mp 128-130 $^\circ C$ (Methanol). IR (KBr): v_{max} 1096, 1265, 1396, 1449, 1501, 1584, 1661, 1667, 2853, 2924, 2956, 3052 and 3120 cm⁻¹ ¹H (500 MHz, CDCl₃, 25 °C): δ (ppm) 0.87 (t, J = 5 Hz, 6H, -CH₃), 1.26-

DOI: 10.1039/C6TC03350D

ARTICLE

Published on 27 September 2016. Downloaded by UNIVERSITY OF NEW ORLEANS on 29/09/2016 15:15:13.

1.52 (m, 28H, -CH₂), 1.72-1.87 (m, 4H, -CH₂), 4.18-4.22 (m, 9H, Fc and -CH₂), 4.43 (s, 2H, Fc), 4.50 (s, 2H, Fc), 6.57 (br, t, *J* = 7.5 Hz, 2H, furanyl C4'-CH and vinyl-CH), 7.03 (d, *J* = 15 Hz, 1H, vinyl- CH), 7.41 (d, *J* = 5 Hz, 1H, furanyl C3'-CH), 8.32 (d, *J* = 5 Hz, 1H, furanyl C3'-CH), 8.32 (d, *J* = 5 Hz, 1H, furanyl C3'-CH), 8.32 (d, *J* = 5 Hz, 1H, furanyl C3-CH) and 9.73 (s, 1H, -CHO). ¹³C NMR (125 MHz, CDCl₃, 25 °C): δ (ppm) 13.09, 21.65, 25.87, 26.31, 28.28, 28.32, 28.34, 28.51, 28.54, 28.59, 28.65, 28.68, 28.73, 29.23, 29.42, 30.61, 30.86, 32.80, 41.76, 41.93, 66.51, 68.58, 69.41, 105.55, 110.16, 110.31, 111.53, 113.04, 118.18, 124.84, 128.43, 131.35, 133.98, 141.73, 147.69, 151.54, 157.27, 159.07, 160.31 and 175.88. HRMS: *m/z* calculated for C₄₇H₅₈FeN₂O₅: 787.3769. Found: 787.3796 (M⁺).

(E)-4-(5-(2,5-didecyl-3,6-dioxo-4-(5-vinylferrocenyl)furan-2-

tetrahydropyrrolo[3,4-c]pyrrol-1-yl)furan-2yl)-2,3,5,6 vl)benzaldehyde 5c Dark blue solid (35 %). Mp 118-120 °C (Methanol). IR (KBr): v_{max} 1096, 1267, 1396, 1587, 1602, 1663, 2853, 2924, 2954 and 3105 cm⁻¹, ¹H (500 MHz, CDCl₃, 25 $^{\circ}$ C): δ (ppm) 0.87 (t, J = 7.5 Hz, 6H, -CH₃), 1.25-1.50 (m, 28H, -CH₂), 1.80-1.86 (m, 4H, -CH₂), 4.17-4.25 (m, 9H, Fc and -CH₂), 4.41 (s, 2H, Fc), 4.49 (s, 2H, Fc), 6.56 (br, t, J = 10 Hz, 2H, furanyl C4'-CH and vinyl-CH), 6.99 (d, J = 15 Hz, 1H, vinyl-CH), 7.13 (d, J = 5 Hz, 1H, furanyl C3'-CH), 7.89 (d, J = 10 Hz, 2H, phenyl-CH), 7.96 (d, J = 10 Hz, 2H, phenyl-CH), 8.37(d, J = 5 Hz, 1H, furanyl C4-CH), 8.44 (d, J = 5 Hz, 1H, furanyl C3-CH) and 10.03 (s, 1H, -CHO). ¹³C NMR (125 MHz, CDCl₃, 25 °C): δ (ppm) 13.10, 21.64, 26.15, 26.36, 28.26, 28.33, 28.47, 28.52, 28.59, 28.68, 28.75, 29.31, 29.40, 30.60, 30.85, 41.73, 41.88, 66.38, 68.53, 69.20, 105.45, 110.03, 110.77, 111.76, 120.36, 123.08, 123.46, 129.49, 130.24, 132.34, 133.60, 134.72, 142.05, 144.48, 153.65, 156.32, 159.47 and 190.15. HRMS: m/z calculated for C₅₃H₆₂FeN₂O₅: 863.4082. Found: 863.4114 (M⁺).

Results and Discussion

Synthesis and characterization

Acetylferrocene 1,⁶⁷ vinylferrocene 3 (Scheme 1),⁶⁸ 3,6-bis-(5bromofuran-2-yl)-2,5-bis-(n-decyl)-pyrrolo[3,4-c]pyrrole-1,4-(2H,5H)-dione **4**⁴² and 5-(4-(5-bromofuran-2-yl)-2,5-bis-(*n*decyl)-3,6-dioxo-2,3,5,6-tetrahydropyrrolo[3,4-c]pyrrol-1yl)furan-2-carbaldehyde 642 were prepared according to literature reports. The intermediate 4-(5-(4-(5-bromofuran-2yl)-2,5-didecyl-3,6-dioxo-2,3,5,6-tetrahydropyrrolo[3,4c]pyrrol-1-yl)furan-2-yl)benzaldehyde 7 was synthesized by the Suzuki coupling⁷⁶ of **4** with 4-formylphenylboronic acid in the presence of Pd(0) as catalyst (Scheme 1). Dipolar dyads 5a-c were synthesized by the Heck reaction⁷⁷⁻⁷⁸ of suitable precursors. Dyad (E)-3-(5-bromofuran-2-yl)-2,5-didecyl-6-(5vinylferrocenyl)furan-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)dione 5a was synthesized by the Heck reaction of 3,6-bis-(5bromofuran-2-yl)-2,5-bis-(n-decyl)-pyrrolo[3,4-c]pyrrole-1,4-(2H,5H)-dione 4 and vinylferrocene 3 in the presence of

palladium (II) acetate, triphenylphosphine and triethylamine as base in toluene (dried over sodium/benzophenone ketyl) as solvent (Scheme 1). Using similar reaction conditions, dyads **5b** and **5c** were obtained by the Heck reaction of vinylferrocene **3** with 5-(4-(5-bromofuran-2-yl)-2,5-bis-(*n*-decyl)-3,6-dioxo-2,3,5,6-tetrahydropyrrolo[3,4-*c*]pyrrol-1-yl)furan-2carbaldehyde **6** and 4-(5-(4-(5-bromofuran-2-yl)-2,5-didecyl-

3,6-dioxo-2,3,5,6-tetrahydropyrrolo[3,4-c]pyrrol-1-yl)furan-2yl)benzaldehyde **7**, respectively (Scheme 1). All compounds were characterized using spectral techniques such as ¹H NMR, ¹³C NMR (Figures S23-S34, ESI†) and HRMS data.

Thermogravimetric analysis

Stability to high processing temperatures often encountered during the device fabrication as well as to counter high pulse power of the laser during the HRS measurements are the prerequisite for the possible applications in electrooptic devices. TGA was performed to determine thermal stability of the dyads **5a-c** and the results are in presented in Figure S1 (See ESI⁺). It is evident that the dyads **5a-c** are thermally stable up to 300 °C, after which significant weight loss is observed. **UV-visible absorption studies**

The dyads **5a-c** exhibit intense low energy (LE) bands in the region 450-750 nm, attributed to intramolecular charge transfer (ICT) between Fc donor and DPP acceptor unit, ^{48,79-86} as well as less intense high energy (HE) bands in the region 250-450 nm, attributable to $\pi \rightarrow \pi^*$ transitions⁸⁶ (Figure 2). As a characteristic feature, the UV-visible absorption spectra are representative of DPP unit in which the LE (MLCT) and HE (ILCT) bands of pristine Fc have been merged. The broad nature of these bands showed that there is extensive mixing of



Scheme 1. Synthesis of intermediates and dyads 5a-c.

Please do not adjust margins Journal of Materials Chemistry C



Figure 2. Overlay of UV-visible absorption spectra of DPP-dyads **5a-c** in dichloromethane (1 x 10^{15} M at 298 K).

various absorption bands, which has been resolved by performing the band fitting analysis (Table 1, Figures S2-S4, ESI⁺).

The observed red shift in the LE ($\Delta\lambda$ = 40 nm, Table 1) as well as HE ($\Delta\lambda$ = 21 nm) bands reflected the effect of increased acceptor strength ($Br \rightarrow CHO$) on moving from **5a** to **5b**, which was further corroborated by the smaller band gap in 5b compared to 5a (Table 2) due to stabilisation of both HOMO and LUMO, the latter more than the former (Table 2, Figure S5, ESI⁺). However, owing to extended π -conjugation (insertion of phenyl ring) in 5c, the HE band showed a blue shift ($\Delta\lambda$ = 48 nm) compared to **5b** (Table 1), while the shift in the LE band in **5c** was only minor ($\Delta\lambda$ = 6 nm) (Table 1). This blue shift is attributed to the increased band gap in 5c compared to 5b (Table 2, Figure S5, ESI⁺), which is also corroborated by the position of the bands calculated by TD-DFT calculations (Table 1). Additionally, from the magnitude of the observed blue shifts of the HE and LE bands, these have been assigned as $\pi \rightarrow \pi^*$ and MLCT transitions, respectively. The MLCT nature of the LE bands was further confirmed from the spectro-electrochemical data of the dyads 5a-c. It was observed that upon electrochemical oxidation, the oscillator strength of the LE bands in all three dyads decreases whereas the oscillator strength of HE band is not significantly affected (Figure 3 and Figure S6-S7, ESI⁺).

Comparison of **5a** with **5c**, revealed a red shift in LE bands $(\Delta\lambda = 34 \text{ nm})$ and a blue shift $(\Delta\lambda = 27 \text{ nm})$ in the HE bands in **5c**, reflecting the combined effect of increasing π -conjugation as well as strength of acceptor in the latter on the $\pi \rightarrow \pi^*$ (HE) and MLCT (LE) transitions, respectively (Table 2, Figure S5, ESI⁺), although the effect of latter is more dominating. Further, the effect of acceptor (-CHO) attached directly to the DPP unit in **5b** is more pronounced than that in **5c** in which a phenyl ring is inserted between the DPP unit and -CHO groups. The linear experimental optical data is in good agreement with the theoretical data. (Figure S8, ESI⁺) The contours of the frontier molecular orbitals (FMOs) of HOMO-LUMO orbitals suggest that the band gap is modulated by both the strength of acceptor as well as the length of π -

 Table 1. UV-visible absorption bands (experimental, band fitted and theoretical) of DPP cores (4,6) and dipolar dyads 5a-c.

	$\lambda_{exp}(nm)^a \in (M^{-1}cm^{-1})$		λ _{fit} (nm) ⁶	$\lambda_{\text{theor}}(\text{nm})^{c}$	
	HE	LE	HE	LE	HE	LE
	band	band	band	band	band	band
4	362	552	-	-	-	-
	346	551 (sh)	-	-	-	-
	278	-	-	-	-	-
6	362	574	-	-	-	-
	330	532 (sh)	-	-	-	-
	310	-	-	-	-	-
5a	404	606	406	612	409.14	553.75
	(12200)	(55100)				
	379	558 (sh)	386	576	363.55	499.29
	(13100)	(38800)				
	332	-	339	-	325.77	-
	(16600)					
5b	428	640	427	652	434.86	665.82
	(6300)	(32800)				
	398	594 (sh)	397	611	408.12	587.07
	(5700)	(26000)				
	328	-	331	-	396.60	-
	(15300)					
5c	387	640	379	646	418.38	653.23
	(16800)	(52900)				
	360	586 (sh)	354	605	367.98	586.25
	(23100)	(36400)				
	286	-	290	-	321.20	-
	(17800)					

^{*a*}Recorded at 1 x 10⁻⁵ M in DCM. ^{*b*}Band fitting was done using Origin Pro8. ^{*c*}Calculated by TD-DFT at B3LYP/6-31G/CPCM model in DCM as solvent (Gaussian 09). Molar extinction coefficients, \in (M⁻¹cm⁻¹) are shown in brackets.

conjugation (Figure S5, ESI⁺). Tables S2 and S3 (ESI⁺) represent the energies of sets of HOMOs and LUMOs obtained from TD-DFT results in both solvent (DCM) as well as gas phases. From the orbital energy level diagram (Figure S9, ESI⁺), it is clear that the LUMO energy levels are more affected than the HOMO counterparts upon changing the strength of acceptor as well as the length of π -conjugation. The energy gap between the LUMO-LUMO+1 (Δ E= 1.28873, **5a**; 1.1388, **5b** and 0.82696, **5c**, Table S2, ESI⁺) is greater than the energy

Table 2. Comparison of experimental (CV/UV-visible absorption) and the calculated (TD-DFT) HOMO-LUMO energy data of 5a-c.

	Exp	erimental d	lata	TD-DFT calculations ^{α}			
	Е _{номо} (eV) ^b	E _{LUMO} (eV) ^c	E ^{g optical} (eV) ^d	Е _{номо} (eV) gas/ DCM phase	E _{LUMO} (eV) gas/ DCM phase	ΔE (eV) gas/ DCM phase	
5a	-4.8667	-2.9952	1.8715	-4.88417/ -5.04199	-2.66182/ -2.83162	2.22235/ 2.21037	
5b	-4.8625	-3.1252	1.7373	-5.08635/ -5.16962	-3.04387 -3.15734	2.04248/ 2.01228	
5c	-4.8500	-3.0661	1.7839	-4.92853/ -5.02268	-2.88359/ -2.98074	2.04494/ 2.04194	

^aUsing TD-DFT/B3LYP/6-31G level. ^bCalculated as $E_{HOMO} = -e[E_{ox}^{onset} + 4.4]$. ^cCalculated as $E_{LUMO} = E_g^{optical} + E_{HOMO}$. ^dCalculated as $E_g^{optical} = 1239.84187/\lambda_{onset}$.

This journal is © The Royal Society of Chemistry 20xx



recorded at 1×10^{-5} M in dichloromethane. (B) Expanded spectroelectrochemical curve of **5a**.

difference between HOMO-HOMO-1 (ΔE = 0.48328, **5a**; 0.68178, **5b** and 0.50341, **5c**, Table S2, ESI⁺), indicating that the LUMO levels are stabilized more than the HOMOs. However, formyl acceptor (directly linked to DPP core) in **5b** has more effect on the energies of LUMO than in **5c** (phenyl ring is inserted between DPP and formyl group).

The concentration dependence of the absorption bands of the dyads was also checked, suggesting that all the dyads follow Beer-Lambert law (Figures S10-S12, ESI⁺) as well as confirms their intramolecular nature. Further, it is interesting to note that although the position of the LE bands of the dipolar dyads **5b** and **5c** is exactly the same, the molar extinction coefficient of LE band in **5c** is almost 2.6 fold more than that of **5b** (Figure 2), although the latter has greater influence of the formyl acceptor group linked directly to the DPP unit. Also, the calculated oscillator strength of LE bands is greater than that of HE bands (Table S4, ESI⁺), supporting the experimentally observed higher molar extinction coefficient of LE bands (Figure 2, Table 1).

Further, on the basis of TD-DFT calculations (B3LYP/6-31G/DCM),⁷⁵ tentative assignment of the electronic transitions involved in the LE and HE bands has been made (Table S4, ESI⁺) and the contour plots of the respective orbitals are shown in figures S13-S18 (See ESI⁺). In the dipolar dyads 5a-c, electron density is mainly located uniformly on the Fc, alkene and DPP sub-units in HOMO whereas in LUMOs, the electron density is shifted towards the acceptor part including the DPP sub-units. The electron density maps (Figure S19, ESI+) also revealed the higher electron density at the DPP and the acceptor units and lesser electron density on the donor part, indicating the drift of electron density from $D \rightarrow A$. It is further evident that the LE and HE bands are composed of mixed electronic transitions. As a general rule, the LE bands in 5a-c are assigned as $D \rightarrow A$ CT transition (MLCT) with some contributions from $\pi \rightarrow \pi^*$ transitions, while additional contribution from $M \rightarrow Cp$ ring transitions are likely to be involved in 5a and 5c. However, the HE bands in both 5a and **5b** is mainly due to $\pi \rightarrow \pi^*$ transition as well as intra-ligand CT (ILCT) within the DPP unit with minor contributions from $D \rightarrow A$ CT transition. Whereas the HE bands in 5c are mainly due to $D \rightarrow A$ CT transitions as electron density is shifted from donor (Fc and alkene unit) towards the acceptor (DPP and -CHO group) with some contributions from $\pi \rightarrow \pi^*$ transitions and ILCT transitions within DPP motif (Figure S18, ESI⁺). Thus, it DOI: 10.1039/C6TC03350D Journal Name

could be expected that in **5c**, both HE and LE bands participate in the charge transfer process.

Solvatochromism, which reflects a change in dipole moment, assessed from the difference in polarity of the ground and excited state is an established tool for the qualitative assessment of the NLO activity of chromophores. However, as literature precedence⁸⁶⁻⁸⁸ attests, the solvatochromism in DPP chromophores is fluctuating in nature. Thus in **5a-c**, no regular trend was observed (Table S5, ESI+), an observation that matches our earlier report.⁴² The blue shift in LE CT bands with increasing the polarity of solvents indicate that the ground state is both more polar and more stabilized as compared to the excited state, which could be due to electrostatic dipoledipole interactions which stabilize ground state more than the excited state.⁸⁹ Thus, it could be suggested that there is more charge-transfer in the ground state, represented by the two mesomeric forms, aromatic (5b) and quinoidal (5b' and 5b") structures (Figure 4). Also, the polar solvents undergo hydrogen bonding with the available lone pairs and hence stabilize ground state more than the excited state.⁸⁷ All solvents considered together, it could be concluded that the dyads 5a-c exhibited irregular but matching solvatochromism. The dominating negative solvatochromism meant that the wavelength of absorption maxima decreased with increasing solvent polarity, indicative of dipole inversion or decreased polarity of the excited state.

Electrochemical studies

Electrochemistry was performed in DCM (freshly distilled from CaH₂), with 2 x 10^{-2} M TBAPF₆ (Aldrich, Electrochemical grade) as a supporting electrolyte. A platinum electrode was used both as working as well as counter electrode and Ag/AgCl as reference electrode. N₂ gas blanket was maintained over the solution during the experiments. Fc was used as an internal reference. Variation in scan rates had minimal effect on peak potentials as well as in E_{1/2} values, which are taken as the halfway point between the forward and reverse peak for each reversible redox process.

Compared to the Fc, dyads **5a-c** exhibited three reversible oxidation peaks (Figure 5). However, reduction peaks were not observed in the cathodic region even upon giving enough reduction potential (upto -2.0 V). Further, during spectroelectrochemistry (Figure 3 and Figures S6-S7, ESI⁺), the gradual diminishing of oscillator strength of the LE band of



Figure 4. Depiction of possible quinoid like structures of dyad 5b.



Figure 5. Cyclic voltammograms of 5a-c (1 x 10^{-4} M in dichloromethane).

5a-c indicated facile oxidation of Fc. Among the oxidation peaks, the one at lower oxidation potential corresponded to Fc sub-unit whereas other two peaks at higher oxidation potential were due to DPP unit. Compared to Fc, the dyads 5a**c** exhibited anodic shift in the first oxidation potential ($\Delta E_{1/2}$ = 0.037V, Fc \rightarrow 5a; $\Delta E_{1/2}$ = 0.043V, Fc \rightarrow 5b and $\Delta E_{1/2}$ = 0.034V, $Fc \rightarrow 5c$, Table 3), indicating that there is increased electronic communication between Fc and DPP unit. The lower electron density at the Fc unit due to the presence of stronger acceptor results in the inhibition of oxidation of Fc. On increasing the acceptor strength from $5a \rightarrow 5b$ (Br \rightarrow CHO), anodic shift in $E_{1/2}$ values is observed in the latter ($\Delta E_{1/2}$ = 0.006, 0.103 and 0.112 V, $5a \rightarrow 5b$, Table 3), which indicate the increased electronic communication between donor and acceptor. This anodic shift could be attributed to stabilization of HOMO energy levels in 5b (TD-DFT calculations, Table 2) although the experimentally calculated energies of HOMO in both 5a and 5b are nearly identical. Further cathodic shift in $E_{1/2}$ values is observed on increasing the length of π -conjugation from **5b** \rightarrow **5c** ($\Delta E_{1/2}$ = 0.009, 0.133 and 0.153 V, $\textbf{5b}{\rightarrow}\textbf{5c},$ Table 3) reflecting a decreased electronic communication between donor and acceptor sub-units, an observation, which is in accordance with increased energy of the HOMO in 5c compared to 5b (Table 2).

Table 3. Electrochemical data for Fc and 5a-c in CH ₂ Cl ₂ .							
Dyad	E _{pa} (V)	E _{pc} (V)	E _{1/2} (V) ^a	i _{pa} (A) ^b	i _{pc} (A) ^b		
Fc	0.530	0.432	0.481	-1.595E-6	1.594E-6		
5a	0.562	0.475	0.518	-1.073E-6	8.436E-7		
	0.946	0.849	0.897	-1.040E-6	7.797E-7		
	1.295	1.225	1.260	-2.82E-06	-3.27E-7		
5b	0.565	0.483	0.524	-6.386E-7	5.140E-7		
	1.045	0.955	1.000	-6.888E-7	4.209E-7		
	1.401	1.343	1.372	-1.93E-06	-2.76E-07		
5c	0.562	0.468	0.515	-5.144E-7	5.234E-7		
	0.911	0.824	0.867	-5.782E-7	4.549E-7		
	1.279	1.159	1.219	-6.820E-7	2.043E-7		

^{*a*}Half-wave potential, $E_{1/2} = (E_{pc} + E_{pa})/2$, where E_{pc} and E_{pa} correspond to the cathodic and anodic peak potentials, respectively; $\Delta E_p = 80-120$ mV; and a scan rate of 100 mV s⁻¹. ^{*b*}Amplitudes of the anodic and cathodic peaks.

On comparing the dyad **5a** with **5c** bearing strong formyl acceptor group as well as enhanced π -conjugation, the latter exhibited cathodic shift ($\Delta E_{1/2}$ = 0.003, 0.03 and 0.041 V, **5a** \rightarrow **5c**, Table 3), indicative of the influence of the directly attached CHO group on the DPP core in **5b**. This cathodic shift could be attributed to the increased energy of HOMO in **5c** (Table 2).

Quadratic hyperpolarizability

In order to make selection of the wavelength for recording second order nonlinear polarizability, β of **5a-c**, fluorescence emission spectra of 5a-c were recorded. It was observed that excitation of the λ corresponding to HE band led to fluorescence emission at wavelength region in excess of 460 nm (Figures S20-S22, ESI⁺). Thus, the second-order nonlinear optical polarizability, β of **5a-c** was measured using femtosecond (≈120 fs) pulsed Insight[®] DS+ laser system at 900 nm using HRS method⁶⁹⁻⁷⁴ under ambient conditions. Measurements at 900 nm ensured minimizing the effect of resonance enhancement on the second-order nonlinear polarizability values.⁹⁰⁻⁹¹ The correction for multi-photon induced fluorescence was obtained by fitting the obtained spectra and only extracting the HRS peak (FWHM 7-8 nm). Selfabsorption of the signal at second harmonic wavelength was corrected using the Lambert-Beer law. Due to the higher accuracy of the HRS set up, chloroform (CHCl₃) was used as solvent as well as reference.

Upon increasing the acceptor strength from **5a** \rightarrow **5b**, β_{HRS} increases (Table 4) as was already inferred from the red shift in the LE (MLCT band) (Table 1, Figure 2). This increase in β_{HRS} could be attributed to increased dipole moment (Table 4) as well as decreased band gap in **5b** (Table 2) although the oscillator strength (*f*, Table S4, ESI⁺) of the MLCT bands of both the dyads is nearly the same. Compared to **5a**, dyad **5c** has both longer π -conjugation and a stronger acceptor (CHO). The higher β_{HRS} in **5c** also reflects higher dipole moment (Table 4), decreased band gap (Table 2) and higher oscillator strength (*f*, Table S4, ESI⁺) of LE MLCT band in **5c**. These observations are in consonance with the two-level model of Oudar and Chemla⁹²⁻⁹³ (equation 1):

Where, β = second-order nonlinear polarizability.

 $\Delta\mu_{ge}\text{=}$ difference in excited state and ground state dipole moments.

 r_{ge} = transition dipole moment, which can be directly correlated to oscillator strength (*f*) or molar extinction coefficient (\in).

 E_{ge} = LE CT transition band gap.

However, an interesting observation is made upon comparing β_{HRS} of **5b** and **5c**. The greater β_{HRS} value of **5c** seems to offset the insulating effect of the phenyl group linking DPP and CHO, compared to **5b**, which recorded lower β_{HRS} (Table 4), although the CHO group is directly attached to the DPP core, as well as the greater dipole moment (Table 4). The higher β_{HRS} of **5c**

Page 8 of 10

Table 4.	Dipole	moment	(μ,	Debye)	and	quadratic	nonlinear	optical
parameters	(eta) of 5a	а-с.						

Dyads	μ ^α TD- DFT gas/DCM	β _{HRS} ^b (10 ⁻³⁰ esu)	β ₂₂₂ ^c (10 ⁻³⁰ esu)
5a	3.8997/	115	280
	5.1871		
5b	8.2456/	150	360
	10.7598		
5c	7.8465/	231	560
	9.4893		

^{*a*}Calculated using TD-DFT/B3LYP/6-31G level. ^{*b*}Second-order nonlinear polarizability, β_{HRS} , recorded at 900 nm in CHCl₃. ^{*c*}Second-order nonlinear polarizability recorded along molecular z-axis.

could be attributed to higher oscillator strength (*f*, Table S4, ESI⁺) of the LE (MLCT) bands as well as participation of both HE and LE absorption bands in charge transfer, both bands represent mainly D \rightarrow A CT transitions (Figures S17-S18, ESI⁺). As the dyads **5a-c** are dipolar in nature and are thus expected to possess large nonlinearities in one direction i.e. mainly along the molecular z-axis, the second-order nonlinear hyperpolarizability was also calculated along the single dominating charge-transfer axis, referred as β_{zzz} tensor component, $\beta_{zzz} = \beta_{HRS}(35/6)^{1/2}$.

To find the figure of merit, β_{HRS} of the dyads **5a-c** were compared with structurally related dyads (8a and 8b, Figure 6) in which DPP core and the Fc donor are linked via alkyne bridge.⁴² It is quite evident from the UV-visible absorption data that alkene bridged dyads 5a-c exhibited red shifted LE (MLCT) bands (Table 1) compared to the alkyne bridged dyads 8a and **8b** (Table 5) and were thus expected to show higher β_{HRS} values. However, the $\beta_{\rm HRS}$ value of **8a** (Table 5) is nearly 1.38 times that of 5b (Table 4), irrespective of the fact that both 8a and 5b have nearly identical dipole moments (µ= 10.7598, 5b and 10.5140, 8a) as well as optical energy band gaps (ΔE = 2.01228, 5b and 2.08248, 8a). The higher second-order nonlinear polarizability of 8a could be attributed to the higher oscillator strength of LE (MLCT) band (f = 1.8460) compared to **5b** (*f* = 0.8508). The marginally higher β_{HRS} of **5c** compared to 8a is not suggestive of the effect of replacing an alkyne (8a) with alkene (5c), but is attributable to the extended π conjugation (insertion of phenyl ring) in the latter (Table 4 and Table 5). Thus, replacement of alkyne link with alkene in Fc-DPP based D- π -A- π -A' chromophores may not be purported as a good strategy to obtain enhanced β_{HRS} as suggested in literature. Likewise, to account for the observed higher β_{HRS} of 5c (Table 4) compared to (not exclusively comparable) 8b (Table 5), it is proposed that the higher dipole moment



Figure 6. Second-order nonlinear optical polarizability of 8a and 8b.

Table 5. Linear, nonlinear optical parameters and TD-DFT results of dyads ${\bf 8a}$ and ${\bf 8b}.^{42}$

Dyads	μ gas phase/ DCM [°]	λ ^{exp b} λmax	fª	ΔE (eV) (Exp./Calc.)	β _{HRs} ^c (10 ⁻³⁰ esu)		
8a	8.6296/	602	1.846	1.913/	207		
	10.5140		0	2.08248			
8b	3.7068/	580	0.683	2.066/	173		
	4.3492			2.22946			
$a_{\rm Llsing}$ TD DET calculations at P2LVD/6.21C $b_{\rm Descarded}$ at 1 x 10 ⁻⁵ M in							

^{*a*}Using TD-DFT calculations at B3LYP/6-31G. ^{*b*}Recorded at 1 x 10⁻⁵ M in DCM. ^{*c*}Recorded at 840 nm in THF. Exp.- experimentally deduced from UV-visible data. Calc.- calculated from TD-DFT.

(μ= 9.4893, **5c** and 4.3492, **8b**), smaller optical band gap (ΔE= 2.04194, **5c** and 2.22946, **8b**) and higher oscillator strength (*f* = 1.2955, **5c** and 0.683, **8b**) of **5c** compared to the alkyne counterpart **8b** might be the deciding factors. In the pair, **8b** (alkyne) and **5a** (alkene), bearing identical DPP units, **8b** (Table 4) depicts greater $β_{HRS}$, irrespective of the fact that both possess marginally different dipole moments (μ= 4.3492, **8b** and 5.1871, **5a**), oscillator strength (*f* = 0.683, **8b** and 0.8644, **5a**) and optical band gap (ΔE= 2.22946, **8b** and 2.21037, **5a**), and replacing alkyne with alkene in **5a** did not lead to a higher $β_{HRS}$.

Conclusions

To sum up, we have described synthesis of new Fc-DPP dyads 5a-c with alkene as linker and recorded their first hyperpolarizabilities by femtosecond HRS technique using femtosecond (120 fs) pulsed laser light system at 900 nm at ambient temperature. All the dyads exhibited structure dependent first hyperpolarizabilities, β_{HRS} . On the basis of UVvisible absorption, electrochemical and TD-DFT studies, a good structure-polarization relationship has been established to account for the observed trends in first hyperpolarizabilities. The linear and nonlinear optical properties are modulated both by the strength of acceptor as well as the length of π conjugation bridge, although the effect of former is more prominent. However, the influence of acceptor is greater when formyl group is directly attached to the DPP core (compare 5b and **5c**). Interestingly, **5c** exhibited higher $\beta_{\rm HRS}$ than **5b** due to the participation of both HE and LE bands in charge transfer in former thus counteracting the insulating effect of phenyl ring linking DPP and formyl group. Further, TGA analysis revealed that the dyads were thermally stable up to 300 °C, which is important in view of the high processing temperatures used during device fabrication. Compared to the Fc, dyads 5a-c exhibited three reversible oxidation peaks with the one at lower oxidation potential corresponding to Fc sub-unit whereas other two peaks at higher oxidation potential are due to DPP unit. The observed anodic shift in the first oxidation potential, indicating that there is increased electronic communication between Fc and DPP unit. The shifts in the anodic and cathodic peak potentials corresponded to the structural changes. The dyads exhibited non-zero dipole moments, indicating their dipolar non-centrosymmetric nature

Journal of Materials Chemistry C Accepted Manuscrip

Journal Name

and hence non-zero β_{HRS} . To find the figure of merit, β_{HRS} of the dyads **5a-c** were compared with structurally related dyads (**8a** and **8b**) in which DPP core and the Fc donor are linked via alkyne bridge.⁴² It is interesting to observe that the replacement of alkyne link with alkene in Fc-DPP based chromophores may not be considered as a good strategy to obtain enhanced β_{HRS} . On the basis of thermal stability as well as the observed β_{HRS} , these dyads could be considered as promising contestants for their applications in electrooptic devices.

Acknowledgements

We are thankful to SERB-DST, New Delhi for the project SB/S1/OC-45/2013 as well as CSIR-New Delhi for research fellowships to SK (09/254 (0240)/2012-EMR-I). NVS is thankful to Ph.D fellowship from Flemish Fund for Scientific Research (FWO-V).

Notes and references

- 1 P. N. Prasad and D. J. Williams, Introduction to Nonlinear Optical Effects in Molecules and Polymers, p 307, Wiley, New York, 1991.
- 2 M. Kivala and F. Diederich, Acc. Chem. Res., 2009, 42, 235-248.
- 3 L. R. Dalton, J. Phys. Condens. Matter., 2003, 15, R897-R934.
- 4 F. Bures, W. B. Schweizer, J. C. May, C. Boudon, J.-P. Gisselbrecht, M. Gross, I. Biaggio and F. Diederich, *Chem. Eur. J.*, 2007, **13**, 5378-5387.
- 5 J.-M. Raimundo, P. Blanchard, N. G. Planas, N. Mercier, I. L. Rak, R. Hierle and J. Roncali, *J. Org. Chem.*, 2002, **67**, 205-218.
- 6 D. S. Chemla and J. Zyss, *Nonlinear Optical Properties of Organic Molecules and Crystals,* Vol. 1, p 482, Academic Press: Orlando, FL, 1987.
- 7 E. Goovaerts, W. Wenseleers, M. H. Garcia and G. H. Cross, *In Handbook of Advanced Electronic and Photonic Materials and Devices*, H. S. Nalwa, Vol. 9, Chapter 3, p 127, Academic Press: San Diego, CA, 2001.
- 8 M. P. Cifuentes and M. G. Humphrey, J. Organomet. Chem., 2004, 689, 3968-3981.
- 9 K. A. Green, M. P. Cifuentes, M. Samoc and M. G. Humphrey, Coord. Chem. Rev., 2011, 255, 2530-2541.
- 10 S. R. Forrest and M. E. Thompson, *Chem. Rev.*, 2007, **107**, 923-925.
- 11 R. D. Miller and E. A. Chandross, *Chem. Rev.*, 2010, **110**, 1-2.
- 12 J. L. Bredas and J. R. Durrant, Acc. Chem. Res., 2009, **42**, 1689-1690.
- 13 C. Li, M. Liu, N. G. Pschirer, M. Baumgarten and K. Mullen, Chem. Rev., 2010, **110**, 6817-6855.
- 14 P. Batail, Chem. Rev., 2004, **104**, 4887-4890.
- 15 Y. Ohmori, Laser Photonics Rev., 2009, 4, 300-310.
- 16 J. Zyss, Molecular Nonlinear Optics: Materials, Physics and Devices, Academic Press: Boston, MA, USA, 1994.
- 17 Ch. Bosshard, K. Sutter, Ph. Pretre, J. Hulliger, M. Florsheimer, P. Kaatz and P. Gunter, Organic Nonlinear Optical Materials, Advances in Nonlinear Optics, Vol. 1, Gordon & Breach: Amsterdam, The Netherlands, 1995.
- 18 H. S. Nalwa and S. Miyata, Nonlinear Optics of Organic Molecules and Polymers, CRC Press: Boca Raton, FL, USA, 1997.
- 19 S. R. Marder, Chem. Commun., 2006, 131-134.

- 20 W. Wu, R. Tang, Q. Li and Z. Li, *Chem. Soc. Rev.*, 2015, **44**, 3997-4022.
- 21 M. G. Kuzyk, J. Mater. Chem., 2009, 19, 7444-7465.
- 22 N. J. Long, Angew. Chem., Int. Ed. Engl., 1995, 34, 21-38.
- 23 D. R. Kanis, M. A. Ratner and T. J. Marks, Chem. Rev., 1994,
- 94, 195-242.
 24 S. R. Marder, B. Kippelen, A. K.-Y. Jen and N. Peyghambarian, Nature, 1997, 388, 845-851.
- 25 I. R. Whittall, A. M. McDonagh, M. G. Humphrey and M. Samoc, Adv. Organomet. Chem., 1998, 42, 291-362.
- 26 K. A. Green, M. P. Cifuentes, M. Samoc and M. G. Humphrey, *Coord. Chem. Rev.*, 2011, **255**, 2025-2038.
- 27 B. J. Coe, Chem. Eur. J., 1999, 5, 2464-2471.
- 28 I. Asselberghs, K. Clays, A. Persoons, A. M. McDonagh, M. D. Ward and J. A. McCleverty, *Chem. Phys. Lett.*, 2003, 368, 408-411.
- 29 C. Sporer, I. Ratera, D. R. Molina, Y.-X. Zhao, J. V. Gancedo, K. Wurst, P. Jaitner, K. Clays, A. Persoons, C. Rovira, and J. Veciana, Angew. Chem., Int. Ed., 2004, 43, 5266-5268.
- 30 M. P. Cifuentes, C. E. Powell, J. P. Morrall, A. M. McDonagh, N. T. Lucas, M. G. Humphrey, M. Samoc, S. Houbrechts, I. Asselberghs, K. Clays, A. Persoons and T. Isoshima, J. Am. Chem. Soc., 2006, **128**, 10819-10832.
- 31 M. Samoc, N. Gauthier, M. P. Cifuentes, F. Paul, C. Lapinte and M. G. Humphrey, *Angew. Chem.*, *Int. Ed.*, 2006, **45**, 7376-7379.
- 32 G. T. Dalton, M. P. Cifuentes, S. Petrie, R. Stranger, M. G. Humphrey and M. Samoc, J. Am. Chem. Soc., 2007, 129, 11882-11883.
- 33 L. B. Lecaque, B. J. Coe, K. Clays, S. Foerier, T. Verbiest and I. Asselberghs, *J. Am. Chem. Soc.*, 2008, **130**, 3286-3287.
- 34 A. Wahab, M. Bhattacharya, S. Ghosh, A.G. Samuelson and P.K. Das, J. Phys. Chem. B, 2008, **112**, 2842-2847.
- 35 W. Guan, G.-C. Yang, C.-G. Liu, P. Song, L. Fang, L. Yan and Z.-M. Su, *Inorg. Chem.*, 2008, **47**, 5245-5252.
- 36 N. Gauthier, G. Argouarch, F. Paul, L. Toupet, A. Ladjarafi, K. Costuas, J.-F. Halet, M. Samoc, M. P. Cifuentes, T. C. Corkery and M. G. Humphrey, *Chem.Eur. J.*, 2011, **17**, 5561-5577.
- 37 S. Barlow and S. R. Marder, Chem. Commun., 2001, 1555-1562.
- 38 P. Debroy and S. Roy, Coord. Chem. Rev., 2007, 251, 203-221.
- 39 R. Horikoshi and T. Mochida, Eur. J. Inorg. Chem., 2010, 5355-5371.
- 40 M. D. Ward, Chem. Soc. Rev., 1995, 24, 121-134.
- 41 T. Kuwana, D.E. Bublitz and G. L. K. Hoh, J. Am. Chem. Soc., 1960, 82, 5811-5817.
- 42 S. Kaur, S. Dhoun, G. Depotter, P. Kaur, K. Clays and K. Singh, *RSC Adv.*, 2015, **5**, 84643-84656.
- 43 S. Dhoun, G. Depotter, S. Kaur, P. Kaur, K. Clays and K. Singh, *RSC Adv.*, 2016, 6, 50688-50696.
- 44 S. Qu and H. Tian, Chem. Commun., 2012, 48, 3039-3051.
- 45 B. Walker, J. Liu, C. Kim, G.C. Welch, J.K. Park, J. Lin, P. Zalar, C. M. Proctor, J. H. Seo, G. C. Bazan and T.-Q. Nguyen, *Energy Environ. Sci.*, 2013, 6, 952-962.
- 46 M. J. Robb, S.-Y. Ku, F. G. Brunetti and C. J. Hawker, J. Polym. Sci., Part A: Polym. Chem., 2013, **51**, 1263-1271.
- 47 Y. Li, P. Sonar, S. P. Singh, W. Zeng and M. S. Soh, J. Mater. Chem., 2011, 21, 10829-10835.
- 48 S.-S. Li, K.-J. Jiang, F. Zhang, J.-H. Huang, S.-G. Li, M.-G. Chen, L.-M. Yang and Y.-L. Song, *Org. Electron.*, 2014, **15**, 1579-1585.
- 49 S.-Y. Liu, W.-Q. Liu, J.-Q. Xu, C.-C. Fan, W.-F. Fu, J. Ling, J.-Y. Wu, M.-M. Shi, A. K.-Y. Jen and H.-Z. Chen, ACS Appl. Mater. Interfaces, 2014, 6, 6765-6775.
- 50 Y.-W. Su, S.-C. Lan and K.-H. Wei, *Mater. Today*, 2012, **15**, 554-562.
- 51 T. Beyerlein, B. Tieke, S. F. Lenger and W. Brutting, Synth. Met., 2002, 130, 115-119.

DOI: 10.1039/C6TC03350D

Journal Name

Published on 27 September 2016. Downloaded by UNIVERSITY OF NEW ORLEANS on 29/09/2016 15:15:13.

- 52 D. Cao, Q. Liu, W. Zeng, S. Han, J. Peng and S. Liu, Macromolecules, 2006, 39, 8347-8355.
- 53 A. C. Grimsdale, K. L. Chan, R. E. Martin, P. G. Jokisz and A. B. Holmes, Chem. Rev., 2009, 109, 897-1091.
- 54 S.-L. Suraru, U. Zschieschang, H. Klauk and F. Wurthner, Chem. Commun., 2011, **47**, 1767-1769.
- 55 Y. Qiao, Y. Guo, C. Yu, F. Zhang, W. Xu, Y. Liu and D. Zhu, J. Am. Chem. Soc., 2012, 134, 4084-4087.
- 56 A. K. Palai, J. Lee, S. Das, J. Lee, H. Cho, S.-U. Park and S. Pyo, Org. Electron., 2012, 13, 2553-2560.
- 57 T. L. Chen, Y. Zhang, P. Smith, A. Tamayo, Y. Liu and B. Ma, ACS Appl. Mater. Interfaces., 2011, 3, 2275-2280.
- 58 Y. Lin, L. Ma, Y. Li, Y. Liu, D. Zhu and X. Zhan, Adv. Energy Mater., 2013, 3, 1166-1170.
- 59 Y. Lin, Y. Li and X. Zhan, Adv. Energy Mater. 2013, 3, 724-728.
- 60 S. Qu, W. Wu, J. Hua, C. Kong, Y. Long and H. Tian, J. Phys. Chem. C., 2010, 114, 1343-1349.
- 61 S. Qu, C. Qin, A. Islam, Y. Wu, W. Zhu, J. Hua, H. Tian and L. Han, Chem. Commun., 2012, 48, 6972-6974.
- 62 H. M. Kima and B. R. Cho, J. Mater. Chem., 2009, 19, 7402-7409.
- 63 G. Hennrich, I. Asselberghs, K. Clays and A. Persoons, J. Org. Chem., 2004, 69, 5077-5081.
- 64 L.-T. Cheng, W. Tam, S. R. Marder, A. E. Stiegman, G. Rikken and C. W. Spangler, J. Phys. Chem., 1991, 95, 10643-10652.
- 65 J. Y. Lee, S. B. Suh, and K. S. Kim, J. Chem. Phys., 2000, 112, 344-348
- 66 B. Champagne and B. Kirtman, Chem. Phys., 1999, 245, 213-226.
- 67 M. M. Hale, Creative Commons Attribution License (CC-BY 2.0).
- 68 I. M. Montero, S. Bruna, A. M. G.Vadillo and I. Cuadrado, Macromolecules, 2014, 47, 1301-1315.
- 69 K. Clays and A. Persoons, Phys. Rev. Lett., 1991, 66, 2980-2983.
- 70 K. Clays and A. Persoons, Rev. Sci. Instrum., 1992, 63, 3285-3289.
- 71 K. Clays, A. Persoons and L. De Maeyer, Adv. Chem. Phys., 1994, 85, 455-498.
- 72 K. Clays and A. Persoons, Rev. Sci. Instrum., 1994, 65, 2190-2194.
- 73 G. Olbrechts, R. Strobbe, K. Clays and A. Persoons, Rev. Sci. Instrum., 1998, 69, 2233-2241.
- 74 G. Olbrechts, K. Wostyn, K. Clays and A. Persoons, Opt. Lett., 1999. 24, 403-405.
- 75 M. J. Frisch et al., Gaussian 09, Revision B.01, Gaussian, Inc., Wallingford, CT, 2010. (for complete reference see supporting information.)
- 76 E. Q. Guo, P. H. Ren, Y. L. Zhang, H. C. Zhang and W. J. Yang, Chem. Commun., 2009, 5859-5861.
- 77 Y. Zhu, I. Heim and B. Tieke, Macromol. Chem. Phys., 2006, 207. 2206-2214.
- 78 Y. Gao, G. Feng, T. Jiang, C. Goh, L. Ng, B. Liu, B. Li, L. Yang , J. Hua and H. Tian, Adv. Funct. Mater. 2015, 25, 2857-2866.
- 79 A. D. Hendsbee, J.-P. Sun, L. R. Rutledge, I. G. Hillb and G. C. Welch, J. Mater. Chem. A., 2014, 2, 4198-4207.
- 80 J. B. Lee, K. H. Kim, C. S. Hong, and D. H. Choi, J. Polymer Sci. Part A: Polymer Chem., 2012, 50, 2809-2818.
- 81 C.-Y. Ji, L. Yin, L. Wang, T. Jia, S. Meng, Y. Sun and Y. Li, J. Mater. Chem. C., 2014, 2, 4019-4026.
- 82 Y. Kim, C.-E. Song, A. Cho, J. Kim, Y. Eom, J. Ahn, S.-J. Moon and E. Lim, Mater. Chem. Phys., 2014, 143, 825-829.
- 83 J. Dhar, N. Venkatramaiah, A. Anitha and S. Patil, J. Mater. Chem. C., 2014, 2, 3457-3466.
- 84 Y. S. Park, T. S. Kale, C.-Y. Nam, D. Choi and R. B. Grubbs, Chem. Commun., 2014, 50, 7964-7967.
- 85 Z. Deng, L. Chen, F. Wu and Y. Chen, J. Phys. Chem. C., 2014, 118, 6038-6045.

- 86 R. S. Szabadai, J. R. Barton, K. P. Ghiggino, J. M. White and D. J. D. Wilson, Aust. J. Chem., 2014, 67, 1330-1337.
- 87 S.-H. Choi, O.-T. Kwon, N.-R. Kim, C. Yoon, J.-P. Kim and J.-H. Choi, Bull. Korean Chem. Soc. 2010, 31, 1073-1075.
- S. Lunak Jr., M. Vala, J. Vynuchal, I. Ouzzane, P. Horakova, P. 88 Moziskova, Z. Elias and M. Weiter, Dyes Pigm., 2011, 91, 269-278
- 89 C. Reichardt, Solvents and Solvent Effects in Organic Chemistry, Wiley-VCH, Edition III, 2003.
- 90 K. Clays, G. Olbrechts, T. Munters, A. Persoons, O.-K. Kim and L.-S. Choi, Chem. Phys. Lett., 293, 1998, 337-342.
- 91 G. Olbrechts, K. Wostyn, K.oen Clays, A. Persoons, S. H. Kang and K. Kim, Chem. Phys. Lett., 308, 1999, 173-175.
- 92 J. L. Oudar and D. S. Chemla, J. Chem. Phys., 1977, 66, 2664-2668.
- 93 J. L. Oudar, J. Chem. Phys., 1977, 67, 446-457.