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A facile organolithium route to ferrocene-based triarylmethyl dyes with substantial near IR and NLO properties

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Abstract

A series of triarylmethanol derivatives containing combinations of phenyl, 1-naphthyl, 4-dimethylamino-4′-stilbenyl, ferrocenyl or 4-[2-ferrocenylethenyl]phenyl groups have been prepared by reaction of $4-[4-Me_2NC_6H_4C{=}C]C_6H_4Li$ or $4-[FcC{=}C]C_6H_4Li$ (Fc = ferrocenyl) with ferrocenecarboxaldehyde, ferrocenyl phenyl ketone, methyl ferrocenecarboxylate, 1-naphthyl phenyl ketone, ethyl benzoate or diethyl carbonate. The carbinols readily form the corresponding intensely coloured carbenium ions in acid solution which have significant electronic absorption in the near infrared. Initial studies indicate that they also possess substantial first hyperpolarisabilities.
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1. Introduction

The syntheses of a multitude of ferrocene derivatives have been already reported, and for many of these their non-linear optical (NLO) properties have been measured in attempts to develop materials for photonic applications, see e.g. [1]. The incentives for pursuing this type of research among organometallics in general and metallocenes in particular have been amply explained [2], and since the list of these derivatives can certainly be enriched it appears reasonable to search further for ferrocene derivatives with improved optical properties. Of course, the ferrocene compounds to be considered for this purpose should be those bearing a strong electron-withdrawing group (EWG), in a structural arrangement that allows the EWG to experience the electron releasing effect of the ferrocenyl group [3], and the structural features that might be altered for achieving this goal, therefore, are either the "bridge" connecting the donor and acceptor moieties or just the acceptor moiety for a given bridge, or both. The connecting bridge is usually a chain of sp^2 hybridised carbon atoms [2], where obviously π-delocalization effects are responsible for the transfer of electron density, or chains of silicon atoms with sp^3 hybridization [2b,4], which have been shown to transmit electron density from the donor to the acceptor by a σ delocalization mechanism [5].

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A variety of electron-accepting groups have been employed so far. These include the ordinary EWG's, i.e., –NO$_2$, –CN, –CH=O, –CO$_2$CH$_3$ [6], as well as other, more novel electron-withdrawing functionalities. The latter category contains groups derived from 3-(dicyanomethylidene)-2,3-dihydrobenzothiophene-1,1-dioxide, 1,3-diethyl-2-thiobarbituric acid, 4-methyl-(2-phenyl)-thioflavilium perchlorate [7], the tropylium cation as well as a number of organometallic moieties [8]. A particularly effective EWG was shown to be a tungsten Fischer carbene moiety in conjugation with a ferrocenyl group through four double bonds. In fact, this molecule was shown to exhibit a record high second-order non-linearity and a remarkable solvent effect [6]. In an attempt to assess the effect of a carbenium ion centre on the NLO properties of certain stilbenes, we synthesized a number of triaryl carbinols with stilbenyl chromophores [9], and the NLO properties of the corresponding dyes have been measured by the hyper-Rayleigh scattering (HRS) technique [10]. We are currently interested in the synthesis of organometallic compounds not only as NLO materials but also as near-infrared dyes (NIR) for which similar structural requirements hold. Due largely to advances in the manufacture of laser diodes, NIR dyes have found numerous technological applications in analysis, optical recording, photography, etc [11]. Particularly significant is that biological fluids and tissues are relatively transparent in the region from ca. 700 to 1100 nm and, for this reason, NIR dyes have also attained special interest for their potential applications in clinical chemistry and in photodynamic tumour therapy [12]. In this paper, we describe the extension of our previously reported methodology to the synthesis of triaryl carbinols bearing ferrocenyl groups and report information concerning their electronic spectra. It should be noted that NIR dyes related to the ones reported here have been reported by Sengupta and Sadhukhan [13]. Preliminary measurements of NLO properties have also been made and, significantly, the tris(ferrocenylethenylphenyl)carbenium ion reported here has a very high first hyper-polarizability.

2. Results

2.1. Synthesis

The synthesis of the new ferrocene derivatives involved the use of stilbenyllithiums, **1a** [9] or their ferrocenylethenyl analogues, **2a**. These organolithiums are derived from the readily accessible bromides **1b** and **2b** through a halogen–metal interchange reaction. Reaction of **1a** and **2a** with the appropriate substrate gave carbinols of type **3** or type **4** (Schemes 1 and 2).

Scheme 1.

Scheme 2.

1a : X = Li
1b : X = Br

2a : X = Li
2b : X = Br
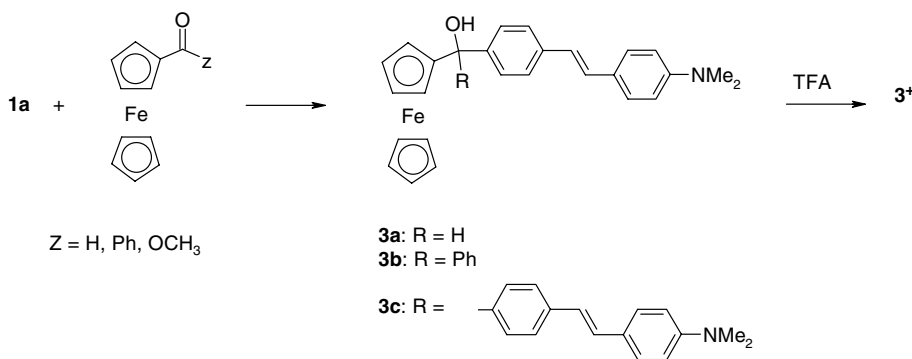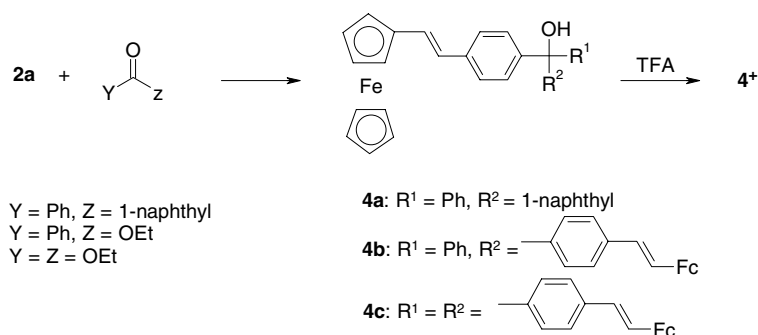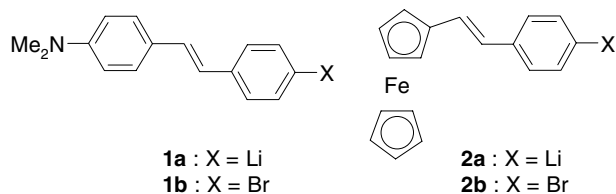
Thus, carbinols have been synthesized with either all the donor moieties being ferrocenyl groups or with mixed donor groups, namely, ferrocenyl and dimethyl-amino groups.

2.2. Optical properties

UV–Vis spectra were recorded both on the carbinols as well as on the corresponding triarylmethyl carbenium dyes, generated in situ by dissolving the carbinols in an acid medium. Tables 1 summarises the NIR absorption maxima and the β values of the compounds. The hyper-Rayleigh scattering technique was employed to measure the NLO properties at a wavelength of 1.06 μm of the triarylmethyl dyes and the results are presented in Table 2.

3. Discussion

Our synthetic method leads to either α-ferrocenyl diarylcarbinols or to ferrocenylethenyl diaryl carbinols, **3** and **4**, respectively, starting from readily accessible

Table 2
First hyperpolarisabilites for triarylcarbinols and triarylcarbenium ions

Compound	[Dye] M[a]	β (10^{-30} esu)[b]	β (10^{-30} esu)[c]
3a	6.86E-5	18 ± 1	200 ± 10
3b	5.81E-5	10 ± 1	320 ± 15
3c	3.94E-5	10 ± 1	260 ± 20
4a	5.38E-6	55 ± 10	400 ± 200
4b	3.22E-6		900 ± 150
4c	2.64E-6		1700 ± 250

[a] Concentration for CF_2HCOOH solution measurements. For the measurements in chlorform, the concentration of carbinol was 0.01 M.
[b] Hyper-Rayleigh scattering at 1.06 μm in chloroform solution.
[c] Hyper-Rayleigh scattering at 1.06 μm in CF_2HCOOH solution.

materials. The yields of carbinols ranged from 38% to 95%. Both types of carbinols in the presence of a sufficiently strong acid are converted to the corresponding carbenium ions, **3**$^+$ and **4**$^+$, with the positively charged carbon atom being either adjacent to the ferrocenyl group or separated from the ferrocenyl group by a 4-ethenyl-phenyl "bridge". Employing di- or tri-fluoroacetic acid in chloroform, we generated stable solutions of the dyes.

The electronic spectra of the dyes exhibit additional bands in the visible region compared to those of the carbinols from which they are derived. These additional bands obviously arise from charge transfer (CT) as well as metal to ligand charge transfer (MLCT), which are the low energy bands [14]. Another general feature of the electronic spectra of the dyes is their dependence on the concentration of the acid. The electronic spectra

Table 1
Electronic spectra of carbinols **3** and **4** – low energy bands and acid concentration dependence

Compound[a]	Solvent[b]	[Dye] M	$\lambda_{max_5}/E_{max_5}$	[CF$_3$COOH] M in CHCl$_3$
3b	CF$_3$COOH (33%)	5.33E-5	710/7501	4.2834
3b	CF$_3$COOH (93%)	2.66E-5	714/4276	12.07
3c	CF$_3$COOH (33%)	5.33E-5	747/9788	4.2834
3c	CF$_3$COOH (66%)	2.66E-5	737/6227	8.5668
3c	CF$_3$COOH (93%)	2.66E-5	775/3075	12.07
4a	CF$_3$COOH (33%)	6.6E-5	1100/17364	4.2834
4a	CF$_3$COOH (66%)	3.33E-5	804/1441	8.5668
4a	CF$_3$COOH (93%)	3.33E-5	804/2340	12.07
4b	CF$_3$COOH (33%)	6.6E-5	1100/13212	4.2834
4b	CF$_3$COOH (66%)	3.33E-5	760/7930	8.5668
4b	CF$_3$COOH (93%)	3.33E-5	744/6430	12.07
4c	CF$_3$COOH (33%)	6.6E-5	786/2515 1100/10090	4.2834
4c	CF$_3$COOH (66%)	1.6E-5	702/11625 1100/1875	8.5668
4c	CF$_3$COOH (93%)	3.2E-5	1100/7437	12.07
4c	CF$_3$COOH (13%)	7.8E-6	1100/61794	1.6874
4c	CF$_3$COOH (19%)	7.3E-6	1100/54704	2.4662
4c	CF$_3$COOH (23%)	6.8E-6	1100/46498	2.9854
4c	CF$_3$COOH (31%)	6.12E-6	1100/23059	4.0238
4c	CF$_3$COOH (33%)	6.0E-6	1100/18999	4.2834

[a] No low energy bands (>500 nm) were observed for carbinol **3a**.
[b] Trifluoroacetic acid (CF$_3$COOH) diluted with chloroform.

of the dyes were recorded by dissolving the carbinols in 4.28, 8.57 and 12.07 M trifluoroacetic acid (TFA) in chloroform. The absorption maxima of the dye derived from the secondary carbinol **3a** exhibited small blue shifts with increasing TFA concentration. Changes occurred also in the absorption intensities. Analogous behaviour was exhibited by the electronic spectra of the dye derived from the tertiary carbinol **3b**, but in this case the low energy band in 12.07 M TFA underwent a small red shift with considerable reduction in its intensity. The dye derived from carbinol **3c** in 12.07 M TFA exhibited a low energy band, absent in the spectra at lower concentrations of TFA. Otherwise the spectra were analogous to the previously discussed cases. The electronic spectra of the dyes derived from carbinols **4a**–**c** with a low concentration of TFA exhibit a low energy strong band with a maximum at 1100 nm. This band is either absent or diminished at higher TFA concentrations. Fig. 1 shows the dependency of the molar extinction coefficient of the low energy band of the dye derived from carbinol **4c** on the concentration of TFA. It can be seen that the $\varepsilon(1100 \text{ nm})$ value decreases rapidly with increasing TFA concentration. It appears reasonable to attribute this effect to the diminishing probability for MLCT with increasing protonation of the iron atom of the ferrocenyl group [15]. In comparing the electronic spectra of the dyes derived from carbinols **3a**–**c** and **4a**–**c**, we conclude that when the positive carbon is adjacent to the ferrocenyl group protonation of the iron atom of the same group is energetically less favourable, whereas when the ferrocenyl group is separated by a 4-ethenylphenyl group from the positively charged carbon atom, protonation of the iron atom of the ferrocenyl group becomes very probable. This effect can be reasonably accounted for by the relative stabilities of the carbenium ions **3**$^+$ and **4**$^+$. The marked stabilization of a carbenium ion centre adjacent to a

ferrocenyl group, such as in **3**$^+$, was noted very early on [16] and has been attributed to a strong interaction of the iron with the electron deficient centre [17]. This could then make iron less prone to undergo protonation. In the case of **4**$^+$, however, the stabilizing effect of iron which is conveyed through the connecting bridge is somewhat attenuated, resulting in a diminished interaction with the carbenium ion centre and thus making the iron atom more susceptible to protonation. These conclusions suggest the direction the synthetic strategy that should follow in order to achieve greater carbenium ion stability as well as improved NIR properties. Namely, the carbenium ion centre should be kept adjacent to the ferrocenyl group and also the moieties providing extended conjugation should be attached directly to the cyclopentadienyl rings. We are currently pursuing this goal.

As far as the NLO properties of the carbinols and the corresponding triarylmethane dyes are concerned, we notice that on ionisation of the secondary carbinol **3a** the β value increases by a factor of 10 (Table 2). An even greater increase is observed in the case of the tertiary carbinol **3b** with one 4-dimethylaminostilbenyl group where the β value increases by a factor of 32, as well as for the tertiary carbinol, **3c**, with two 4-dimethylaminostilbenyl groups, where a 26-fold increase is observed. It appears, therefore, that a second 4-dimethylaminostilbenyl group is less effective in contributing to the NLO properties than a phenyl group. Contrasting behavior is exhibited in the case of the carbinols with ferrocenylethenyl groups. Here we notice that the β value increases rapidly on going from the mono- to di-, to tri-ferrocenylethenyl carbenium compound. It appears, therefore, that there is a rather uniform increase in the difference between the dipole moments of the ground and the excited states on going from mono- to di-, to tri-ferrocenylethenyl carbenium ion. In fact dye **4c** seems to display one of the highest β values measured for an organic compound. However, clearly, these huge values are partly due to strong resonance effects, as both fundamental and harmonic wavelengths (1064 and 532 nm, respectively) used in HRS measurements come close to maxima absorption bands in the near-IR and visible range. But after dispersion corrections, the corresponding "static" $\beta(0)$ values (e.g., for **4c**) are found to be similar (about 100×10^{-30} esu) to that of the parent Crystal Violet molecule ($\beta(0) = 95 \times 10^{-30}$ esu). This confirms the well-established electron donor properties [7] (here similar to those of dialkyamino moieties) of ferrocenyl compounds.

Fig. 1. Dependence of low energy band extinction coefficient for **4c** on TFA concentration.

4. Experimental

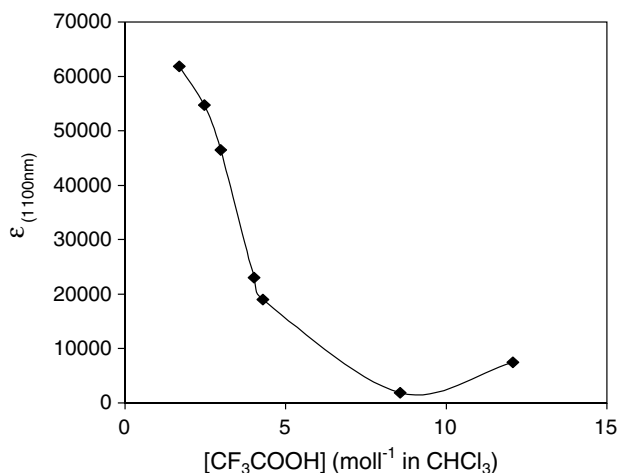The ^{1}H and ^{13}C NMR spectra were performed at 300.13 and 75.04 MHz, respectively, on a Bruker AC

300 instrument. UV–Vis spectra were recorded on a Hitachi Model U-2001. Mass spectrometry was performed using a Finnigan MT TSQ 7000 with electrospray injection (ESI) and GC–MS using a Varian Saturn 2000 with a 30 m × 0.25 m DB5-MS column. Samples of analytical purity were obtained by column chromatography on silica gel (Merck, GEDURAN 60, 0.40–0.063 nm) using as eluent toluene/hexane/ethyl acetate (77/19/4). Elemental analyses were performed at the National Hellenic Research Foundation. Tetrahydrofuran, freshly dried over 9-fluorenylpotassium and, diethyl ether, dried over sodium-benzophenone, and dichloromethane, dried over calcium hydride, were distilled before use. The solution of *n*-butyllithium in methylcyclohexane (1.87 M) was prepared by following the conventional procedure. The starting materials 4-,4′-dimethylaminobromo-(*E*)-stilbene (**1b**) and (*E*)-bromostyrylferrocene (**2b**) were synthesized following a standard Horner–Emmons procedure by condensing, respectively, *p*-dimethylaminobenzaldehyde and ferrocenecarboxaldehyde with *p*-bromobenzyl diethyl phosphonate, using a suspension of sodium hydride in tetrahydrofuran. Recrystallisation from methylcyclohexane in the presence of a small iodine crystal, gave the pure *E*-isomers.

4.1. [4-[2(E)-[4-(dimethylamino)phenyl]ethenyl]-phenyl]ferrocenylmethanol] (3a)

A solution of (**1b**) (2.1 g, 6.95 mmol) in tetrahydrofuran (60 mL) was cooled to −80 °C by means of a liquid nitrogen–acetone bath. Rapid addition of *n*-butyllithium in methylcyclohexane, 1.90 M (4.9 mL, 9.3 mmol) caused the immediate development of a greenish color. The mixture was stirred and warmed slowly to −40 °C during a period of 2 h, resulting in a yellow suspension. The mixture was cooled to −70 °C, and ferrocenecarboxaldehyde, 1.49 g, 6.95 mmol, was added. Cooling was discontinued and the resulting clear orange-red solution was stirred until it reached room temperature. Water (50 mL) and dichloromethane (50 mL) were added and the phases separated. After extraction of the aqueous layer with two other portions of dichloromethane (2 × 50 mL), the organic phases were collected and evaporated to dryness under reduced pressure to afford an orange solid. Recrystallisation from isopropanol afforded the carbinol of compound (**3a**) as orange-brown needles (2.9 g, 6.6 mmol, 95%). m.p.: 94–96 °C. ^{1}H NMR, (300.13 MHz, CDCl$_3$): 2.42 (s, 1H, OH) 2.97 (s, 6H, (CH$_3$)$_2$N); 4.19 (m, 4H, C$_5$H$_4$); 4.22 (s, 5H, C$_5$H$_5$); 5.45 (s, 0.5H, CHO); 5.46 (s, 0.5H, CHO); 6.91 (d, ^3J = 8.7 Hz, 2H); 6.89 (d, ^3J = 16.3 Hz, 1H, −HC=CH−); 7.03 (d, ^3J = 16.3 Hz, 1H, −HC=CH−); 7.39 (m, 5H). ^{13}C NMR, (75.47 MHz, CDCl$_3$): 40.4; 66.0; 67.3; 68.0; 68.4; 71.8; 94.1; 112.4; 124.0; 125.8;

126.4; 127.5; 128.6; 137.3; 141.6; 150.0. UV–Vis (CHCl$_3$) $\lambda_{max}(\varepsilon)$ 240 nm (23 700), 356 nm (49 500). MS, ESI: (M + 1)/438.0, (M + 1 − H$_2$O)/419.9, (M + 1 + Na)/460.0. Anal. Calc. for C$_{27}$H$_{27}$FeNO: C, 74.15; H, 6.22; N, 3.20. Found: C, 73.90; H, 6.25; N, 3.15%. *Carbocation* (**3a$^+$**): UV–Vis (CHCl$_3$/CF$_3$COOH = 1/14) $\lambda_{max}(\varepsilon)$ 275 nm (22 707), 297 nm (22 857), 376 nm (25 037), 432 nm (19 398).

4.2. [4-[2(E)-[4-(dimethylamino)phenyl]ethenyl]-phenyl]phenylferrocenylmethanol (3b)

Prepared as above from 1.5 g, 5.0 mmol, of **1b** in tetrahydrofuran (35 mL), *n*-butyllithium, 1.87 M, 3.5 mL, 6.54 mmol, and ferrocenylphenylketone, 1.44 g, 5.0 mmol to give 1.75 g, 68%, of the title compound as red crystals after purification by column chromatography followed by one recrystallisation from isopropanol. m.p.: 172–174 °C. ^{1}H NMR, (300.13 MHz, CDCl$_3$): 2.98 (s, 6H, (CH$_3$)$_2$N); 3.44 (s, 1H, OH); 4.05 (m, 2H, C$_5$H$_4$); 4.18 (s, 5H, C$_5$H$_5$); 4.27 (s, 2H, C$_5$H$_4$); 6.71 (d, ^3J = 8.4 Hz, 2H); 6.89 (d, ^3J = 16.3 Hz, 1H, −HC=CH−); 7.03 (d, ^3J = 16.3 Hz, 1H, −HC=CH−); 7.27 (m, 7H); 7.47 (m, 4H). ^{13}C NMR, (75.47 MHz, CDCl$_3$): 39.2; 67.1; 67.3; 67.5; 98.1; 111.2; 122.7; 123.9; 124.6; 125.5; 125.7; 126.0; 126.2; 127.4; 135.4; 144.2; 145.7; 148.8; 152.7. UV–Vis (CHCl$_3$) $\lambda_{max}(\varepsilon)$ 239 nm (19 100), 357 nm (41 225). Anal. Calc. for C$_{33}$H$_{31}$FeNO: C, 77.19; H, 6.08; N, 2.72. Found: C, 73.95; H, 6.21; N, 2.58%. *Carbocation* (**3b$^+$**): UV–Vis (CHCl$_3$) $\lambda_{max}(\varepsilon)$ 290 nm (26 256), 398 nm (18 155), 448 nm (18 829), 714 nm (4276).

4.3. Bis[4-[2(E)-[4-(dimethylamino)phenyl]ethenyl]-phenyl]ferrocenylmethanol (3c)

Prepared as above from **1b**, 2.3 g, 7.61 mmol, THF, 60 mL, *n*-butyllithium 1.87 M, 5.6 mL, 10.47 mmol, and ferrocenecarboxylic acid ethyl ester, 1.0 g, 3.86 mmol. The crude product upon purification by column chromatography afforded 1.23 g, 38% of **3c**, as a red-brown powder, m.p.: 250 °C (dec). ^{1}H NMR, (300.13 MHz, CDCl$_3$): 2.97 (s, 6H, (CH$_3$)$_2$N); 3.41 (s, 1H, OH); 4.09 (m, 4H, C$_5$H$_4$); 4.18 (s, 5H, C$_5$H$_5$); 6.69 (d, ^3J = 8.3 Hz, 4H); 6.88 (d, ^3J = 16.1 Hz, 2H, −HC=CH−); 7.02 (d, ^3J = 16.1 Hz, 2H, −HC=CH−); 7.25 (m, 4H); 7.47 (m, 8H). ^{13}C NMR, (75.47 MHz, CDCl$_3$): 40.4; 68.3; 68.6; 68.7; 99.4; 112,4; 124,0; 125,1; 125.8; 127.3; 127.5; 128.6; 136.6; 145.5; 150.1; 155.3. UV–Vis (CHCl$_3$) $\lambda_{max}(\varepsilon)$ 240 nm (23 675), 356 nm (59 200). Anal. Calc. for C$_{43}$H$_{42}$FeN$_2$O: C, 78.29; H, 6.41; N, 4.24. Found: C, 78.34; H, 6.48; N, 4.06%. *Carbocation* (**3c$^+$**): UV–Vis (CHCl$_3$/CF$_3$COOH = 1/14): $\lambda_{max}(\varepsilon)$ 303 nm (28 657), 525 nm (24 156), 569 nm (21 380).

4.4. [4-[2(E)-[ferrocenyl]ethenyl]bromo]benzene (2b)

Prepared by the Horner–Emmons procedure as described above, m.p.:142–143 °C; ^{1}H NMR, (300.13 MHz, CDCl$_3$): 4.13 (s, 5H, C$_5$H$_5$); 4.29 (1s, 2H, C$_5$H$_4$); 4.45 (1s, 2H, C$_5$H$_4$); 6.62 (d, ^3J = 15.8 Hz, 1H, −HC=CH−); 6.86 (d, ^3J = 15.8 Hz, 1H, −HC=CH−); 7.28 (d, ^3J = 8.0 Hz, 2H); 7.43 (d, ^3J = 8.0 Hz, 2H); ^{13}C NMR, (75.47 MHz, CDCl$_3$): 66.8; 69.1; 82.7; 120.1; 124.6; 127.1; 127.8; 131.6; 136.8. UV–Vis (CHCl$_3$) $\lambda_{max}(\varepsilon)$ 236 nm (11 725), 268 nm (7738), 312 nm (24 775). UV–Vis (CHCl$_3$/CF$_3$COOH = 2/1) $\lambda_{max}(\varepsilon)$ 278 nm (18 462), 379 nm (6554), 433 nm (4803), 922 nm (938). Anal. Calc. for C$_{18}$H$_{15}$BrFe: C, 58.90; H, 4.12. Found: C, 58.83; H, 4.05%.

4.5. [4-[2(E)-[ferrocenyl]ethenyl]phenyl]naphthyl-phenylmethanol (4a)

Prepared as above from 2b, 1.84 g, 5.0 mmol, THF 50 mL, n-butyllithium, 1.82 M, 3.8 mL, 6.9 mmol, and 2-naphthylphenylketone, 1.16 g, 5.0 mmol giving a crude product which was purified by recrystallisation from isopropanol and then by column chromatography to give the title compound as a red powder, 1.8 g, 70%. m.p.: 192–194 °C; ^{1}H NMR, (300.13 MHz, CDCl$_3$): 3.31 (s, 1H, OH); 4.13 (s, 5H, C$_5$H$_5$); 4.28 (1s, 2H, C$_5$H$_4$); 4.45 (1s, 2H, C$_5$H$_4$); 6.79 (d, ^3J = 16.3 Hz, 1H, −HC=CH−); 6.88 (d, ^3J = 16.3 Hz, 1H, −HC=CH−); 6.92 (d, ^3J = 7.40 Hz, 2H); 7.33 (m, 11H); 7.81 (d, ^3J = 8.30 Hz, 2H); 8.13 (d, ^3J = 8.60 Hz, 1H). ^{13}C NMR, (75.47 MHz, CDCl$_3$): 66.8; 69.9; 69.1; 83.3; 91.3; 124.20; 125.4; 125.5; 127.1; 127.6; 128.0; 128.7; 129.3; 134.9; 136.6; 141.9; 145.4; 146.9. UV–Vis (CHCl$_3$) $\lambda_{max}(\varepsilon)$ 239 nm (28 240), 272 nm (26 560), 313 nm (34 540), 368 nm (4720), 463 nm (1920). MS ESI: 503.2 (M + 1 − H$_2$O). Anal. Calc. for C$_{35}$H$_{28}$FeO (Mr = 520.46): C, 80.77; H, 5.42. Found: C, 80,71; H, 5.80%. Carbocation (4a$^+$): UV–Vis (CHCl$_3$/CF$_3$COOH = 1/14): $\lambda_{max}(\varepsilon)$ 259 nm (23 470), 297 nm (18 847), 357 nm (14 465), 499 nm (37 515), 621 nm (27 010).

4.6. Bis[4-[2(E)-[ferrocenyl]ethenyl]phenyl] phenylmethanol (4b)

Prepared as above from 2b, 1.84 g, 5.0 mmol, THF, 50 mL, n-butyllithium, 1.82 M, 3.8 mL, 6.9 mmol, and ethyl benzoate, 0.36 mL, 2.5 mmol, affording, after one recrystallisation from isopropanol and column chromatography, compound 4b as a red solid, 1.5 g, 88%. m.p.: 192–194 °C. ^{1}H NMR, (300.13 MHz, CDCl$_3$): 2.77 (s, 1H, OH); 4.14 (s, 10H, C$_5$H$_5$); 4.29 (s, 4H, C$_5$H$_4$); 4.47 (s, 4H, C$_5$H$_4$); 6.70 (d, ^3J = 16.0 Hz, 2H, −HC=CH−); 6.89 (d, ^3J = 16.0 Hz, 2H, −HC=CH=); 7.33 (m, 13H).^{13}C NMR, (75.47 MHz, CDCl$_3$): 66.8; 69.0; 69.1;

81.8; 83.2; 125.2; 125.3; 127.2; 127.8; 127.9; 128.2; 136.8; 145.2; 146.7. UV–Vis (CHCl$_3$) $\lambda_{max}(\varepsilon)$ 239 nm (25 560), 271 nm (31 380), 312 nm (44 780), 374 nm (5640), 461 nm (2460). MS ESI 663.2 (M + 1 − H$_2$O). Anal. Calc. for C$_{43}$H$_{36}$Fe$_2$O (Mr = 680.48): C, 75.9; H, 5.33. Found: C, 75.53; H, 5.37%. Carbocation (4b$^+$): UV–Vis (CHCl$_3$/CF$_3$COOH = 1/14): $\lambda_{max}(\varepsilon)$ 256 nm (25 565), 297 nm (21 562), 378 nm (10 990), 486 nm (33 093), 563 nm (43 123), 744 nm (6430).

4.7. Tris[4-[2(E)-[ferrocenyl]ethenyl]phenyl] methanol (4c)

Prepared as above from 2b, 1.84 g, 5.0 mmol, THF, 50 mL, n-butyllithium, 1.82 M, 3.8 mL, 6.9 mmol, and diethyl carbonate, 0.200 mL, 1.66 mmol, affording the title compound after purification by one recrystallisation from isopropanol and column chromatography as a red solid, 1.0 g, 74%, m.p.: 172 °C (dec). ^{1}H NMR, (300.13 MHz, CDCl$_3$): 2.74 (s, 1H, OH); 4.13 (s, 15H, C$_5$H$_5$); 4.28 (s, 6H, C$_5$H$_4$); 4.46 (s, 6H, C$_5$H$_4$); 6.79 (d, ^3J = 16.2 Hz, 3H, −HC=CH−); 6.88 (d, ^3J = 16.2 Hz, 3H, −HC=CH−); 7.28 (d, ^3J = 8.4 Hz, 6H); 7.38 (d, ^3J = 8.4 Hz, 6H). ^{13}C NMR, (75.47 MHz, CDCl$_3$): 66.8; 69.0; 69.1; 81.7; 83.2; 125.2; 125.3; 127.2; 128.1; 136.8; 145.2. UV–Vis (CHCl$_3$) $\lambda_{max}(\varepsilon)$ 239 nm (38 583), 270 nm (44 583), 316 nm (72 957), 376 nm (10 624), 459 nm (5292). MS ESI 873.2 (M + 1 − H$_2$O). Anal. Calc. for C$_{55}$H$_{46}$Fe$_3$O · H$_2$O: C, 72.67 H, 5.33. Found: C, 72.71; H, 5.26%. Carbocation (4c$^+$): UV–Vis (CHCl$_3$/CF$_3$COOH = 1/14): $\lambda_{max}(\varepsilon)$ = 260 nm (46 562), 439 nm (12 000), 579 nm (78 562).

4.8. Hyper-Rayleigh measurements

The approach followed here relies on harmonic light scattering (HLS) as initially proposed and developed by Terhune and Maker [18]. A transverse single mode Nd^{3+}:YAG laser is used as the fundamental source, consisting of 10 MW peak power, 30 ns duration IR pulses at 1.064 µm repetition rate 10 Hz. The incident IR intensity can be continuously monitored by a half-wave plate rotated between two crossed Glan polarizers. A small part of the incident beam is removed at a low reflection angle by a glass plate and sent onto a highly non-linear NPP (N-4-nitrophenyl-prolinol) powder used as a reference frequency doubler. The emitted second harmonic signal is detected by a photomultplier. The main fundamental beam is focused into the sample using a 8 cm focal length converging lens. The sample consists in an adequately designed parallelepipedic spectrophotometric cell presenting four polished windows so as to allow for simultaneous longitudinal illumination and transverse collection of the scattered emission. Concentrations range from 10^{-6} to 10^{-2} M l^{-1} depending on the solvent: around 10^{-2} M l^{-1} in chloroform where

non-ionized carbinol derivatives display weak β values and a good transparency at both 1.06 and 0.532 μm; between 10^{-6} and 10^{-5} M l^{-1} in difluoroacetic acid where ionized compounds are strongly NLO active, but display some absorption losses at the operating wavelengths. Solutions are preliminary cleaned through 0.5 μm Millipore filters in order to remove most microscopic particles which could otherwise induce breakdowns in the presence of the focused laser beam. Collection of the HLS photons at 532 nm is performed in the transverse off-axis 90° direction, using a large (diameter 50 mm) and short focal distance ($f = 50$ mm) spherical lens in order to focus the light onto the photocathode of a photomultiplier tube. The detected reference and scattered harmonic signals, after spectral selection through an interference filter with 5 nm spectral resolution, are then sampled and averaged using a Stanford Research System Boxcar and processed by a computer. Variation of the scattered second harmonic intensity from the solution is recorded on the computer as a function of the reference second harmonic signal provided by the NPP powder, which scales like the square of the incoming fundamental intensity. Then $\langle \beta^2 \rangle$ and β (defined as $\sqrt{\langle \beta^2 \rangle}$) values are inferred from the slopes of the resulting lines. Calibrations are made with respect to the pure solvent (chloroform or difluoroacetic acid).

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