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Journal of Organometallic Chemistry 691 (2006) 2785–2792
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

New stable, isolable triarylmethyl based dyes absorbing in the near infrared

Carolina Villalonga-Barber, Barry R. Steele *, Veronika Kovač, Maria Micha-Screttas, Constantinos G. Screttas

Institute of Organic and Pharmaceutical Chemistry, National Hellenic Research Foundation, Vas. Constantinou 48, Athens 116 35, Greece

Received 10 January 2006; received in revised form 10 February 2006; accepted 15 February 2006
Available online 6 March 2006

Abstract

A series of new intensely coloured multicharged methylium compounds containing the 4-[2-ferrocenylethenyl]phenyl group and with significant electronic absorption in the near infrared have been prepared via acidification of the tertiary carbinols obtained by reaction of 4-[FcCH=CH]C_6H_4Li with diethyl isophthalate, diethyl terephthalate, diethyl phthalate or the triethyl ester of 1,3,5-benzene carboxylic acid. Even more stable dyes were prepared from two new triarylmethanol derivatives containing 2,6-dimethoxy-4-[2-(ferrocenyl)-ethenyl]phenyl or 2,6-dimethoxy-4-[2-[4-(dimethylamino)phenyl]ethenyl]phenyl groups which were prepared by reaction of 4-[FcCH=CH]-2,6-$MeO_2C_6H_2$Li or 4-[4-$Me_2NC_6H_4$CH=CH]-2,6-$MeO_2C_6H_2$Li (Fc = ferrocenyl) with diethyl carbonate. These carbinols on treatment with acid deposit dark-purple crystals which have been isolated and characterised spectroscopically. They absorb in the near infrared and, whereas their solutions begin to decolourise only after several days, they display long-term stability to air and moisture in the solid state.

Keywords: Near infrared; Carbenium ion; Ferrocenyl; Stilbene

1. Introduction

The present strong scientific and commercial interest in near-infrared (NIR) absorbing dyes ($\lambda_{max} > 700$ nm) arises from their large range of potential applications in optical imaging systems, infrared photography, optical lasers, biological probes, etc. [1,2]. 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 [3].

Dyes for applications in the NIR region require small differences in the energy between the HOMO and LUMO. This situation can be attained by end-capping of conjugated organic chromophores with strong donor and acceptor substituents which allows the possibility of intramolecular charge transfer [4].

Acceptor substituted ferrocenes provide a building-block for the synthesis of organometallic NIR dyes and Hückel calculations have shown that increasing the acceptor strength gives rise to large bathochromic shifts due to a considerable lowering of the already low-lying MLCT transition [5]. The optimal structural arrangement allows the EWG to experience the electron releasing effect of the ferrocenyl group [5a], and this is usually achieved through a chain of sp^2 hybridized carbon atoms [6] where π-delocalization effects are obviously responsible for the transfer of electron density.

A variety of electron-accepting groups have been employed so far. These include conventional EWG's, e.g., $-NO_2$, $-CN$, $-CH=O$, $-CO_2CH_3$ [7], as well as other, rather novel electron-withdrawing functionalities. Since

* Corresponding author. Tel.: +30 2107273873; fax: +30 2107273877.
E-mail address: bsteele@eie.gr (B.R. Steele).

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doi:10.1016/j.jorganchem.2006.02.017

carbocations are the strongest known acceptor groups, and following our previous experience in non-linear optical materials [8] and our recent interest in NIR dyes [9], we set out to asses the accumulative effect of multicharged carbenium ion centres on the NIR properties of certain stilbene derivatives and to examine them in the context of other recent reports of NIR triphenylmethane dyes by Sengupta [10] and Meier [11].

2. Results and discussion

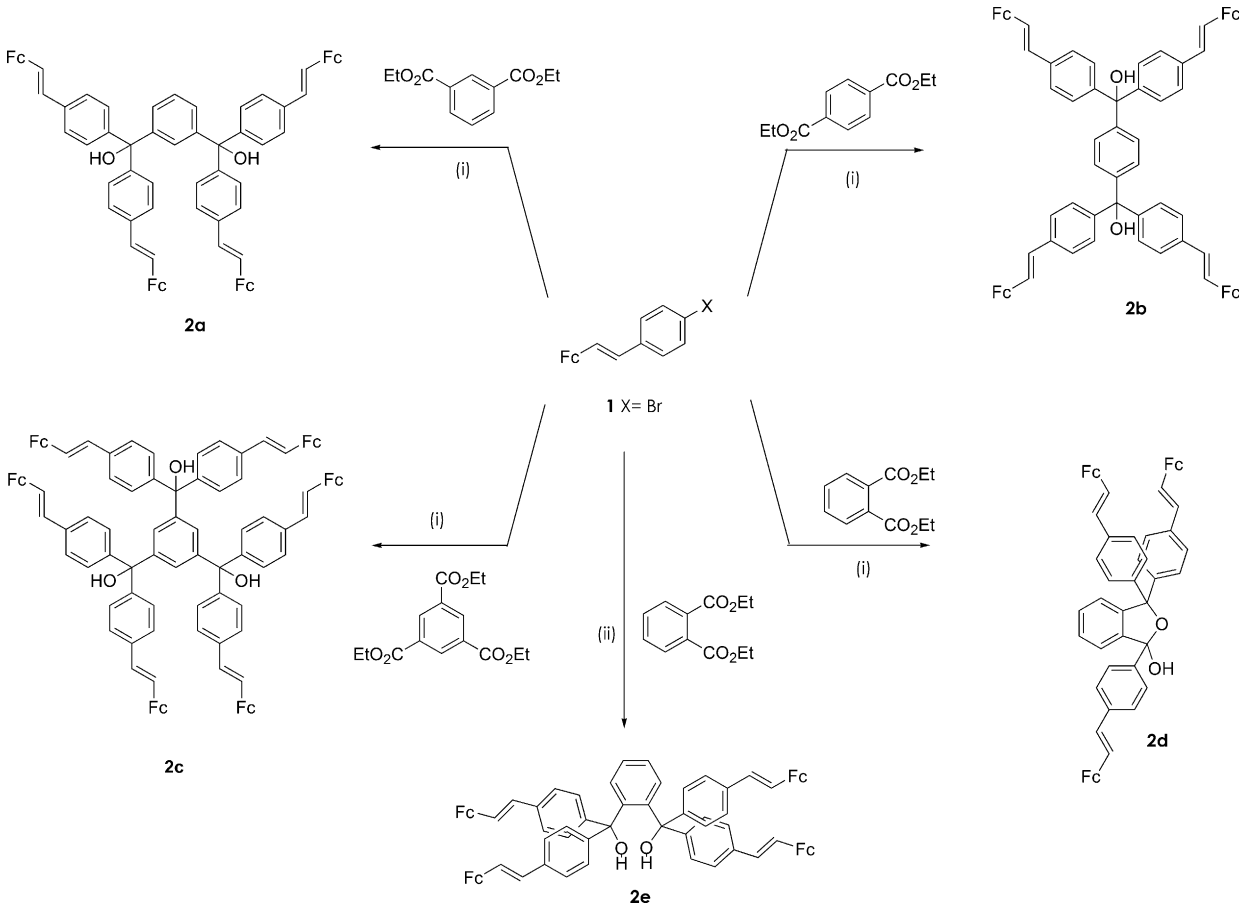
2.1. Preparation of bis and tri{4-[2(E)-(ferrocenyl)ethenyl]phenylhydroxymethyl}benzenes

The synthesis of the new ferrocene derivatives involved the use of the stilbenyllithium derived from the readily accessible bromide **1** through a halogen–metal interchange reaction [9]. Reaction of the in situ generated stilbenyllithium with the appropriate substrate gave carbinols **2a**–**2e** (Scheme 1).

Addition to diethyl phthalate under the same conditions gave lactol **2d** as the sole product. Generation of carbinol **2e** required forcing reaction conditions, i.e., use of a large excess of the organolithium reagent and heating the reaction mixture at reflux for a week (Scheme 1).

UV–Vis spectra were recorded both for the carbinols as well as for the corresponding triarylmethyl dyes generated by dissolving the carbinols in chloroform containing trifluoroacetic acid (TFA). These carbocations could also be generated by addition of 60% aq. HPF_6, as indicated by the intensely coloured solutions obtained (dark blue for **2a**–**c**, dark red for **2d** and **2e**). In contrast to analogous compounds [12], isolation of the above dyes could not be achieved because during aqueous work-up the dyes rapidly revert to their corresponding carbinols. Similar behaviour has been observed by others for similar dyes [13]. Also, compared to the analogous dyes **3a** [10a] and **3b** [9], the dye solutions reported above are highly unstable. Only minutes after preparation, the NIR band decreases in intensity suggesting the solutions to be moisture sensitive.

The electronic spectra of the dyes (see Table 1) exhibit additional bands in the visible region presumably arising from charge transfer (CT) as well as metal-to-ligand charge transfer (MLCT) [14]. Also a small pH dependency was observed so that, when the acid concentration was increased, the NIR band gradually decreased and virtually vanished at high acid concentrations (except for compounds **2d** and **2e** where the opposite occurred). This is likely to be due to the increasing protonation of the iron atoms of the ferrocenyl

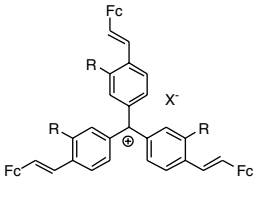


Scheme 1. (i) *n*BuLi, THF, −78 to −65 °C, 1 h then di or triester, THF, −78 °C to r.t., 20 h; (ii) *n*BuLi, Et_2O, 0 °C to r.t, 1 h then diester, Et_2O, 0–40 °C, 1 week.

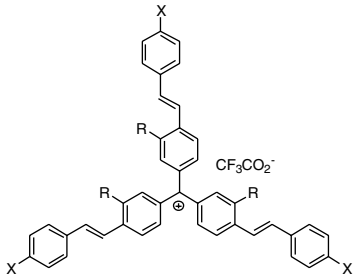
Table 1
Electronic spectra of carbinols **2a**–**2e** and their carbenium ions

Entry	Compound	[dye] M	[TFA] M	λ_{Vis} (log ε)	λ_{NIR} (log ε)
1	**2a**	2.80E-4	–	453 (3.75)	
2	**2a**	1.12E-4	3.11E-1	640 (4.47)	1100 (4.25)
3	**2a**	1.12E-4	5.16E-1	648 (4.35)	1100 (4.10)
4	**2a**	1.12E-4	7.78E-1	650 (4.19)	1100 (3.85)
5	**2a**	1.12E-4	1.29	647 (4.40)	1037 (3.85)
6	**2a**	1.12E-4	2.58	580 (3.40)	1100 (3.94)
7	**2b**	2.80E-4	–	454 (3.70)	
8	**2b**	1.12E-1	3.11E-1	638 (4.50)	1100 (4.28)
9	**2b**	1.12E-1	4.15E-1	648 (4.56)	1100 (4.24)
10	**2b**	1.12E-1	5.16E-1	645 (4.45)	1100 (4.18)
11	**2b**	5.60E-2	7.78E-1	651 (4.32)	1100 (3.95)
12	**2b**	5.60E-2	1.29	651 (4.40)	1100 (3.97)
13	**2b**	5.60E-2	2.58	589 (4.51)	925 (3.74)
14	**2c**	2.50E-4	–	452 (3.69)	
15	**2c**	1.00E-4	3.11E-1	652 (2.47)	1100 (4.15)
16	**2c**	1.00E-4	5.16E-1	649 (3.60)	946 (3.69)
17	**2c**	2.5E-5	1.29	585 (3.57)	914 (3.64)
18	**2c**	1.00E-4	2.58	596 (4.46)	894 (3.66)
19	**2c**	2.5E-5	6.49	602 (4.04)	892 (3.71)
20	**2c**	1.00E-4	7.74	586 (4.50)	848 (3.70)
21	**2d**	4.50E-4	–	453 (3.59)	
22	**2d**	1.81E-4	3.11E-1	523 (4.25)	889 (3.81)
23	**2d**	1.81E-4	5.16E-1	525 (4.29)	895 (4.08)
24	**2d**	1.81E-4	7.78E-1	538 (4.28)	903 (4.07)
25	**2d**	1.81E-4	1.29	542 (4.28)	904 (4.09)
26	**2d**	1.81E-4	5.16	530 (4.29)	926 (4.08)
27	**2e**	3.40E-4	–	453 (3.55)	
28	**2e**	1.36E-4	3.11E-1		911 (3.00)
29	**2e**	1.36E-4	5.16E-1	659 (3.07)	931 (3.20)
30	**2e**	1.36E-4	7.78E-1	659 (3.10)	945 (3.26)
31	**2e**	1.36E-4	1.29	661 (3.20)	9.41 (3.37)
32	**2e**	1.36E-4	2.58	653 (3.27)	939 (3.44)
33	**2e**	1.36E-4	5.16		927 (3.46)

groups [15], which results in a diminishing probability for MLCT [9]. Similar behaviour is found for the related triaryl carbenium salt, **4a** [10b], although a smaller excess of acid is required there for changes in the electronic spectra, indicating that the basicity of an *N*,*N*-dimethylaniline is greater than that of the ferrocenyl group. The anisyl group, like the ferrocenyl group, also induces a weak pH-dependency on the electronic absorption of carbocation **4b** [16].



3a R = Me, X = BF_4^-
3b R= H, X = $CF_3CO_2^-$



4a X = NMe_2, R = Me
4b X= OMe, R = H

It is of interest to note the lower wavelength and lower intensity of the NIR band for carbocations derived from **2d** and **2e** compared to **2a**–**c**. This might be due to crowding around the carbocationic centres preventing the cations from becoming planar and therefore making delocalisation of the charge more difficult.

2.2. Preparation of tris 4-susbstituted-2,6-(dimethoxyphenyl)methanols

We reasoned that the introduction of some bulkiness around the carbocationic centre would prevent the nucleophilic attack of water molecules and would therefore result in more stable carbenium ions. It was also thought that the substitution of the *ortho* positions of the triaryl carbenium core with strong electron donor groups would, through resonance, stabilize the carbocation centre.

It is known that *ortho* methoxy groups in phenyl derivatives give unusual physical and chemical properties to the derivatives due to the steric and electronic effects of the substituents and Wada [17] has demonstrated that the number of methoxy substituents on phenyl groups influences the stability and reactivity of triphenylcarbenium salts while the greater basicity of tris-2,6-dimethoxyphenylmethanol compared to that of triphenylmethanol has been known for some time [18].

Considering this stability factor, we prepared ferrocene derivative **6a** and the analogue **6b** for comparison with the triarylmethanol derivatives that we had synthesised previously [19]. The synthetic routes are similar to the preparation of derivatives **2a**–**2e**. Thus *ortho*-directed lithiation of stilbenes **5a** and **5b** by *n*-butyllithium followed by addition of diethyl carbonate gave triarylmethanols **6a** and **6b**, respectively (Scheme 2).

Stilbene derivatives **5a** and **5b** were prepared through Horner–Emmons procedures by condensing, respectively, ferrocenecarboxaldehyde and *p*-dimethylaminobenzaldehyde with diethyl 3,5-dimethoxyphenylphosphonate. The latter was prepared from 3,5-dimethoxybenzylalcohol following the procedure described by Marder [20].

Carbinols **6a** and **6b** reacted with a slight excess of 60% aqueous hexafluorophosphoric acid to give the carbenium salts **7a** and **7b**, respectively, which could be isolated as dark blue crystals which were stable to air and moisture. The electronic spectrum of **7a** was recorded in chloroform, thus allowing comparison with those reported above, but **7b** was insoluble in this solvent and so the spectrum was recorded in acetonitrile.

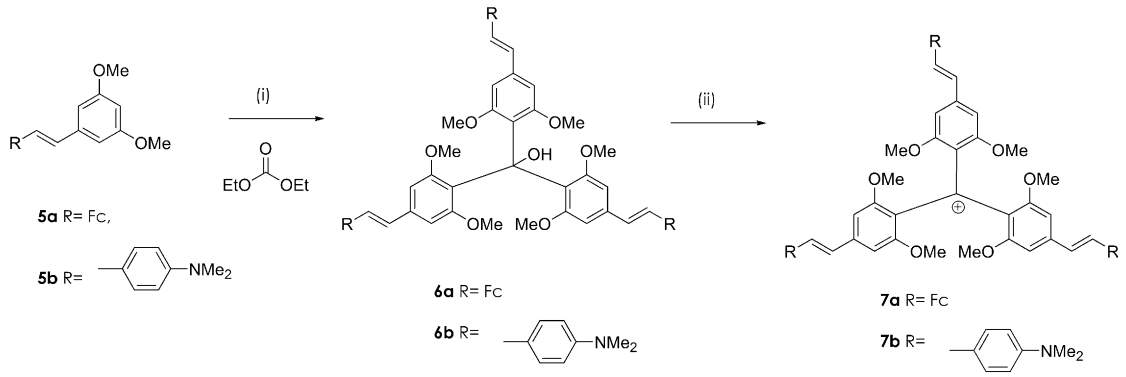
Dye **7a** exhibits strong additional bands in the visible and in the NIR region compared to carbinol **6a**. A similar slight pH dependent behaviour was found to that of dyes derived form carbinols **2a**–**2e**, (Table 2) where the NIR band virtually disappears at very high acid concentrations (entry 7, Table 2)

It is worth mentioning that, one week after the preparation of the samples for UV measurements, some changes were observed. The solution of **6a** in chloroform in the absence of acid (entry 1, Table 1) had turned from orange to dark blue and its electronic spectrum now resembled that of the carbenium salt **7a**, with an absorption in the NIR region ($\lambda_{max} = 904$ nm). This suggests the facile formation of the carbenium ion **7a** from the carbinol even at neutral conditions, resembling behaviour already observed for tris(2,6-dimethoxyphenyl)methanol [17]. On the other hand, the solutions corresponding to entries 2–7 of Table 2 had all lost their colour intensity and the NIR band had disappeared. Their UV spectra were all similar but did not resemble that of the carbinol **6a**. A possibility could be that the carbenium salt is reduced to the corresponding triarylmethane, a reaction known to be possible in solvents such as alcohols, diethyl ether or tetrahydrofuran [17]. Although this is still to be confirmed for our compound, it might be plausible due to the small traces (0.6–1%) of ethanol present in the HPLC grade chloroform used for our dilutions. An alternative possibility is that the changes are the result of photooxidation which is known to occur for ferrocene derivatives in halocarbon solvents [21]. The solution of **7a** in chloroform was relatively more stable and after a week the electronic spectrum was similar to that recorded initially ($\lambda_{max} = 907$ nm, $\log \varepsilon = 4.10$). However, after a longer period of time (ca. 5 months) the spectra again resemble those of week-old samples for entries 2–7 and presumably the reasons for this are similar to those mentioned above.

Table 2
Electronic spectra of carbinol **6a** and carbenium ion **7a**

Entry	Compound	[dye] M	[TFA] M	λ_{Vis} ($\log \varepsilon$)	λ_{NIR} ($\log \varepsilon$)
1	**6a**	3.70E-4	–	452 (3.59)	
2	**6a**	3.70E-5	5.19E-2	643 (4.18)	914 (4.29)
4	**6a**	3.70E-5	2.59E-1	635 (4.25)	920 (4.35)
5	**6a**	3.70E-5	1.29	620 (4.35)	950 (4.15)
6	**6a**	3.70E-5	6.49	622 (4.36)	926 (3.86)
7	**6a**	3.70E-5	11.7	645 (4.35)	–
8	**7a**	8.30E-5	–	638 (4.05)	900 (4.17)

Dye **7b** also exhibited a band in the NIR region, but this spectrum could not be compared to that of the carbinol **6b** from which it is derived since the carbocation forms readily as indicated by the electronic spectrum with a characteristic band at 845 nm (in acetonitrile). This band has a small molar extinction coefficient ($\log \varepsilon = 2.31$) indicating a low concentration of the carbocation in the fresh solution of **6b**. As time progresses, however (just a few hours), light yellow chloroform solutions of **6b** turn deep blue and the NIR band goes off scale, suggesting the facile formation of the carbenium ion **7b** at neutral conditions. The acetonitrile solution was more stable and no colour change was appreciable to the eye after a few hours, although the NIR band had slightly increased in intensity ($\log \varepsilon = 2.46$). The absorption spectra of the dye show strong pH depen-



Scheme 2. (i) *n*BuLi, Et_2O, 0 °C to r.t, 20 h then diethyl carbonate, Et_2O, 0–40 °C, 48 h. (ii) HPF_6, EtOH.

Table 3
Electronic spectra of carbinol **6b** and carbenium ion **7b** (in acetonitrile)

Entry	Compound	[dye] M	[TFA] M	λ_{vis} (log ε)	λ_{NIR} (log ε)
1	**6b**	4.10E-4	–	393 (3.81)	845 (2.31)
2	**6b**	9.10E-5	6.50E-3		893 (4.48)
3	**6b**	4.10E-5	1.30E-2	543 (3.86)	811 (4.63)
4	**6b**	4.10E-5	5.19E-2	563 (4.02)	798 (4.46)
5	**6b**	4.10E-5	1.29	571 (4.19)	675 (4.48)
6	**6b**	4.10E-5	6.49	660 (4.48)	
7	**7b**	4.80E-5	–	–	833 (4.54)

dent behaviour similarly to that of **4a** [10b]. At low acid concentrations the NIR band was the predominant one. In strongly acidic solution, however, this band disappeared and a lower wavelength band became the major one (Table 3). This has been observed for analogous systems and can be attributed to the formation of the *N*-protonated dye **7b**H^+ [10b].

The solutions corresponding to entries 2 and 7 do not experience a very substantial change over time. The NIR band loses intensity and also blue shifts slightly ($\lambda_{max} = 888$ $\log\varepsilon = 4.46$ after one week and $\lambda_{max} = 843$ $\log\varepsilon = 4.06$ after 5 months for solution in entry 2 and $\lambda_{max} = 792$ $\log\varepsilon = 4.24$ after 5 months for solution in entry 4). This indicates that the specific samples were relatively stable especially compared to the corresponding ferrocenyl derivative in which, as mentioned previously, the solvent may be implicated in the appearance of secondary reaction products [17,21].

3. Experimental

3.1. General

All reactions requiring dry or inert conditions were carried out in flame dried equipment under an atmosphere of argon. Solvents were dried under argon by conventional methods. Reactions were monitored by TLC using commercially available Merck Kieselgel 60 F_{254}. After aqueous work-up of reactions mixtures, organic solutions were routinely dried over anhydrous sodium sulphate. Column chromatography was carried out on Kieselgel 60 (particle size 40–63 μm) as supplied by Merck. NMR spectra were recorded in solutions of $CDCl_3$ unless stated otherwise on a Bruker AC 300 spectrometer operating at 300.13 MHz for ^1H and 75.04 MHz for ^{13}C. Chemical shifts are reported in ppm relative to residual $CHCl_3$ (δ_H 7.27) or to $CDCl_3$ (δ_C, central line of triplet: 77.0). Coupling constants (*J*) are given to the nearest 0.5 Hz. UV–Vis spectra were recorded on a Hitachi Model U-2001. Mass spectrometry was performed using a Finnigam MT TSQ7000 with electrospray injection (ESI) and GC–MS using a Varian Saturn 2000 with 30 m × 0.25 m DB5-MS column. Elemental analyses were performed at the National Hellenic Research Foundation using a Perkin–Elmer PE2400 II analyser.

The solution of *n*-butyllithium in methylcyclohexane was prepared by following the conventional procedure. Sodium hydride (60% in mineral oil) was washed with dry hexane before use. The starting material (*E*)-bromostyrylferrocene (**1**) was synthesized as previously described [9].

3.2. 1,3-bis{4-[2(E)-(ferrocenyl)ethenyl]phenylhydroxymethyl}benzene (**2a**)

A solution of **1** (1.7 g, 4.6 mmol) in tetrahydrofuran (30 mL) was cooled to −78 °C by means of a liquid nitrogen–acetone bath. Rapid addition of *n*-butyllithium (2.3 mL, 4.3 mmol; 1.87 M in methylcyclohexane) caused the immediate appearance of a precipitate. The mixture was stirred and warmed slowly up to −65 °C. After 1 h the mixture was re-cooled to −78 °C and a solution of diethyl isophthalate (171 mg, 0.77 mmol) in tetrahydrofuran (3 mL) was added. Cooling was discontinued and the resulting solution was left stirred overnight. NH_4Cl (sat. solution) (15 mL) was added and the solution concentrated. Dichloromethane (20 mL) was added and the phases separated. After extraction of the aqueous layer with two other portions of dichloromethane (2 × 20 mL), the organic phases were collected and evaporated to dryness under reduced pressure to afford an orange solid. Recrystallization from chloroform and hexane afforded carbinol **2a** as an orange-red solid (877 mg, 88%). m.p.: 270 °C (dec.). ^1H NMR ($CDCl_3$): 7.50–7.10 (m, 4H, Ar—H × 4), 7.32 (d, *J* 8.0, 8H, Ar—H × 8), 7.20 (d, *J* 8.0, 8H, Ar—H × 8), 6.85 (d, *J* 15.0, 4H, CH=×4), 6.65 (d, *J* 15.0, 4H, CH=×4), 4.48 (s, 8H, Fc—H × 8), 4.30 (s, 8H, Fc—H × 8), 4.15 (s, 20H, Cp × 4) and 2.71 (s, 2H, OH × 2). ^{13}C NMR ($CDCl_3$): 146.3, 145.3, 136.7, 128.1, 127.5, 127.4, 127.2, 126.7, 125.7, 125.4, 83.9 (C, quat.), 81.8 (C, quat.), 69.6 (Cp), 69.4 (Fc—CH) and 67.0 (Fc—CH). UV–Vis ($CHCl_3$) λ_{max}(log ε) 453 nm (3.75). MS (ESI) *m/z* (%): 1284.1 ([M+H]$^+$, 10%), 1283.1 (M$^+$, 10), 641.8 (30), 344.1 (90) and 287.9 (100). Calc. for $C_{80}H_{66}Fe_4O_2$: C, 74.91; H, 5.19. Found: C, 74.99; H, 5.15%.

3.3. 1,4-bis{4-[2(E)-(ferrocenyl)ethenyl]phenylhydroxymethyl}benzene (**2b**)

Prepared as above from **1** (1.8 g, 4.9 mmol), *n*-butyllithium (2.4 mL, 4.5 mmol; 1.87 M in methylcyclohexane) and diethyl terephthalate (180 mg, 0.80 mmol) to give the title compound as an orange-red solid after recrystallization from chloroform and hexane (940 mg, 91%). m.p.: 250 °C (dec.). ^1H NMR, (THF-d^8): 7.38 (d, *J* 8.5, 8H, Ar—H × 8), 7.26 (d, *J* 8.5, 12H, Ar—H × 12), 6.90 (d, *J* 16.0, 4H, CH=×4), 6.71 (d, *J* 16.0, 4H, CH=×4), 5.41 (s, 2H, OH × 2), 4.46 (s, 8H, Fc—H × 8), 4.22 (s, 8H, Fc—H × 8) and 4.07 (s, 20H, Cp × 4). ^{13}C NMR (THF-d^8): 147.6, 147.4, 137.4, 129.1, 128.1, 127.5, 126.5, 125.7, 84.5 (C, quat.), 81.5 (C, quat.), 69.8 (Cp), 69.6 (Fc—CH) and 67.6 (Fc—CH). UV–Vis ($CHCl_3$) λ_{max}(log ε) 454 nm (3.70). MS (ESI) *m/z* (%): 1283.8 ([M+H]$^+$, 65%), 1282.1 (M$^+$, 40), 642.3 (100), 641.4 (90) and 287.9 (60). Calc. for

$C_{80}H_{66}Fe_4O_2$: C, 74.91; H, 5.19. Found: C, 74.82; H, 5.25%.

3.4. 1,3,5-tri{4-[2(E)-(ferrocenyl)ethenyl]phenylhydroxymethyl}benzene (**2c**)

Prepared as above from **1** (2.25 g, 6.1 mmol), *n*-butyllithium, (4.3 mL, 5.7 mmol; 1.35 M in methylcyclohexane) and triethyl ester 1,3,5-benzene tricarboxylic acid (200 mg, 0.68 mmol) to give the title compound as an orange-red solid after recrystallization from chloroform and hexane (900 mg, 70%). m.p.: >300 °C (dec.). ^{1}H NMR, (THF-d^8): 7.38 (s, 3H, Ar—H × 3), 7.27 (d, *J* 8.0, 12H, Ar—H × 12), 7.16 (d, *J* 8.0, 12H, Ar—H × 12), 6.90 (d, *J* 16.0, 6H, CH=×6), 6.71 (d, *J* 16.0, 6H, CH=×6), 5.40 (s, 3H, OH × 2), 4.46 (s, 12H, Fc—H × 12), 4.23 (s, 12H, Fc—H × 12) and 4.00 (s, 30H, Cp × 6). ^{13}C NMR (THF-d^8): 147.9 (Ar—C, quat.), 147.1 (Ar—C, quat.), 137.1 (Ar—C, quat.), 129.2 (CH), 127.3 (CH), 126.8 (CH), 125.6 (CH), 84.5 (C, quat.), 81.8 (C, quat.), 69.8 (Cp), 69.6 (Fc—CH) and 67.6 (Fc—CH). UV–Vis ($CHCl_3$) $\lambda_{max}(\log\varepsilon)$ 453 nm (3.69). MS (ESI) *m*/*z* (%): 1885.4 ($[M+H]^+$, 60%), 1884.2 (M^+, 50), 943.2 (100) and 942.4 (100). Calc. for $C_{117}H_{96}Fe_6O_3$: C, 74.55; H, 5.13. Found: C, 74.64; H, 5.12%.

3.5. 1,3,3-tri{4-[2(E)-(ferrocenyl)ethenyl]phenyl}-1,3-dihydro-isobenzofuran-1-ol (**2d**)

Prepared as above from **1** (1.7 g, 4.6 mmol), *n*-butyllithium, (2.3 mL, 4.3 mmol; 1.87 M in methylcyclohexane) and diethyl phthalate (171 mg, 0.77 mmol) to give the title compound as an orange-red solid after recrystallization from chloroform and hexane (755 mg, 98%). m.p.: 165 °C (dec.). ^{1}H NMR, ($CDCl_3$): 7.65–7.25 (m, 16H, Ar—H × 16), 6.87 (d, *J* 16.0, 3H, CH=×3), 6.67 (d, *J* 16.0, 3H, CH=×3), 4.47 (s, 6H, Fc—H × 6), 4.29 (s, 6H, Fc—H × 6), 4.14 (s, 15H, Cp × 3) and 3.0 (s, 1H, OH). ^{13}C NMR ($CDCl_3$): 144.3 (Ar—C, quat.), 143.3 (Ar—C, quat.), 142.9 (Ar—C, quat.), 142.6 (Ar—C, quat.), 140.9 (Ar—C, quat.), 137.8 (Ar—C, quat.), 137.2 (Ar—C, quat.), 137.0 (Ar—C, quat.), 129.2 (CH), 128.6 (CH), 128.0 (CH), 127.4 (CH), 127.3 (CH), 126.2 (CH), 125.6 (CH), 125.5 (CH), 123.8 (CH), 123.3 (CH), 107.8 (C, quat.), 92.7 (C, quat.), 83.3 (Fc-C, quat.), 69.2 (Cp), 69.1 (Fc—CH) and 66.8 (Fc—CH). UV–Vis ($CHCl_3$) $\lambda_{max}(\log\varepsilon)$ 453 nm (3.59). MS (ESI) *m*/*z* (%): 995.5 ($[M+H]^+$, 10%), 994.5 (M^+, 15), 574.2 (50), 497.4 (20) and 287.9 (30). Calc. for $C_{62}H_{50}Fe_3O_2$: C, 74.87; H, 5.07. Found: C, 74.91; H, 5.04%.

3.6. 1,2-bis{4-[2(E)-(ferrocenyl)ethenyl]phenylhydroxymethyl}benzene (**2e**)

n-Butyllithium (5.5 mL, 7.5 mmol; 1.35 M in methylcyclohexane) was added to a solution of **1** (2.9 g, 8.0 mmol) in diethyl ether (40 mL) at 0 °C. The mixture was stirred and allowed to warm up to r.t. during a period of 1 h. It was then recooled to 0 °C and a solution of diethyl phthalate (222 mg, 1.0 mmol) in diethyl ether (3 mL) was added. Cooling was discontinued and the resulting solution was warmed up to reflux temperature for one week. NH_4Cl (sat. solution) (15 mL) was added and the solution concentrated. Dichloromethane (20 mL) was added and the phases separated. After extraction of the aqueous layer with two other portions of dichloromethane (2 × 20 mL), the organic phases were collected and evaporated to dryness under reduced pressure to afford an orange solid. Recrystallization from diethyl ether and hexane afforded carbinol **2e** as an orange-red amorphous solid (1.0 g, 78%). ^{1}H NMR ($CDCl_3$): 7.60–7.00 (m, 4H, Ar—H × 4), 7.37 (d, *J* 8.0, 8H, Ar—H × 8), 7.12 (d, *J* 8.0, 8H, Ar—H × 8), 6.89 (d, *J* 15.0, 4H, CH=×4), 6.71 (d, *J* 15.0, 4H, CH=×4), 4.47 (s, 8H, Fc—H × 4), 4.29 (s, 8H, Fc—H × 4) and 4.15 (s, 20H, Cp × 4). ^{13}C NMR ($CDCl_3$): 146.9 (Ar—C, quat.), 144.4 (Ar—C, quat.), 136.7 (Ar—C, quat.), 133.4 (CH), 128.2 (CH), 127.2 (CH), 126.0 (CH), 125.5 (CH), 125.3 (CH), 84.2 (C, quat.), 83.3 (C, quat.), 69.2 (Cp), 69.0 (Fc—CH) and 66.8 (Fc—CH). UV–Vis ($CHCl_3$) $\lambda_{max}(\log\varepsilon)$ 453 nm (3.55). MS (ESI) *m*/*z* (%): 1284.1 ($[M+H]^+$, 30%), 1283.1 (M^+, 20), 641.8 (50), 344.1 (80) and 287.9 (100). Calc. for $C_{80}H_{66}Fe_4O_2$: C, 74.91; H, 5.19. Found: C, 74.98; H, 5.17%.

3.7. Diethyl 3,5-dimethoxyphenylphosphonate

To a mixture of 3,5-dimethoxybenzylalcohol (17.4 g, 103 mmol) in triethyl phosphite (80 mL) was added iodine (28.8 g, 113 mmol) at 0 °C slowly. After stirring for 5 min the mixture was heated to 150 °C for 3 h. The excess triethyl phosphite was distilled out under vacuum. The remaining liquid was purified by distillation under vacuum to give the title compound as a clear oil (26.7 g, 89.5%). bp: 130–140 °C/0.1 mbar. ^{1}H NMR ($CDCl_3$): 6.43 (s, 2H, Ar—H × 2), 6.43 (s, 1H, Ar—H), 4.10–3.90 (m, 4H, $P(OCH_2CH_3)_2$) 3.74 (s, 6H, OMe × 2), 3.06 (d, J_{H-P} 21.5, 2H, CH_2—P) and 1.23 (t, *J* 7.0, 6H, Me × 2); ^{13}C NMR ($CDCl_3$): 160.6 (Ar—C, quat.), 133.4 (Ar—C, quat., d, J_{C-P} 7.5), 107 (Ar—CH, d, J_{C-P} 5.0), 98.9 (Ar—CH), 62.1 ($P(OCH_2CH_3)_2$, d, J_{C-P} 7.5), 55.1 (OMe), 33.8 (CH_2—P, d, J_{C-P} 140) and 16.2 (Me); MS (EI) *m*/*z* (%): 288 (M^+, 288%) and 273 (100).

3.8. (E)-1-2-(ferrocenylethenyl)-3,5-dimethoxybenzene (**5a**)

A solution of diethyl 3,5-dimethoxyphenylphosphonate (11.8 g, 41.0 mmol) in tetrahydrofuran (50 mL) was added to a suspension of sodium hydride (4.5 g, 112.2 mmol; 60% in mineral oil) in tetrahydrofuran (20 mL) at r.t. The mixture was allowed to stirred for 1 h before adding a solution of ferrocenecarboxaldehyde (8.0 g, 37.4 mmol) in tetrahydrofuran (30 mL). After stirring the reaction mixture at reflux temperature for 18 h, methanol was added and the

solvent evaporated. The residue was redissolved into dichloromethane (80 mL), washed with brine (50 mL), dried and evaporated. The crude product was recrystallized from isopropanol to give the title compound as an orange solid (10.6 g, 81%). m.p.: 109—112 °C. ^{1}H NMR ($CDCl_3$): 6.86 (d, *J* 16.0, 1H, CH=), 6.63 (d, *J* 16.0, 1H, CH=), 6.60 (d, *J* 2.0, 2H, Ar—H × 2), 6.37 (t, *J* 2.0, 1H, Ar—H), 4.46 (s, 2H, Fc—H × 2), 4.29 (s, 2H, Fc—H × 2), 4.15 (s, 5H, Cp) and 3.84 (s, 6H, OMe × 2). ^{13}C NMR ($CDCl_3$): 160.9 (Ar—C, quat.), 139.9 (Ar—C, quat.), 127.5 (CH), 125.8 (CH), 103.8 (CH), 99.1 (CH), 82.9 (Fc—C, quat.), 69.2 (Cp), 69.0 (Fc—CH), 66.9 (Fc—CH) and 55.3 (OMe). MS (ESI) *m*/*z* (%): 348.1 (M^+, 100).

3.9. N,N-dimethyl-4-[(E)-2-(3,5-dimethoxyphenyl)ethenyl] benzeneamine (**5b**)

Prepared as above from 3,5-dimethoxyphenylphosphonate (10.0 g, 35.4 mmol), sodium hydride (3.8 g, 95 mmol; 60% in mineral oil) and 4-dimethylaminobenzaldehyde (4.7 g, 31.5 mmol) to give the title compound as a dark yellow solid after recrystallization from isopropanol (6.0 g, 67.5%). m.p.: 82–84 °C. ^{1}H NMR ($CDCl_3$): 7.44 (d, *J* 8.5, 2H, Ar—H × 2), 7.06 (d, *J* 16.0, 1H, CH=), 6.83 (d, *J* 16.0, 1H, CH=), 6.73 (d, *J* 8.5, 2H, Ar—H × 2), 6.67 (d, *J* 2.0, 2H, Ar—H × 2), 6.37 (t, *J* 2.0, 1H, Ar—H), 3.85 (s, 6H, OMe × 2) and 3.00 (s, 6H, NMe_2). ^{13}C NMR ($CDCl_3$): 160.8 (Ar—C, quat.), 150.1 (Ar—C, quat.), 140.1 (Ar—C, quat.), 129.3, 127.6, 125.3, 124.2, 112.3, 103.9, 99.1, 55.3 (OMe) and 40.4 (NMe_2). MS (ESI) *m*/*z* (%): 284.1 ($[M+H]^+$, 20%), 283.1 (M^+, 100) and 266 (50).

3.10. Tris {2,6-dimethoxy-4-[2-(E)-(ferrocenyl)ethenyl]-phenyl}methanol (**6a**)

n-Butyllithium (1.8 mL, 2.51 mmol; 1.40 M in methylcyclohexane) was added to a suspension of **5a** (1.0 g, 2.87 mmol) in diethyl ether (150 mL) at 0 °C. The mixture was allowed to warm up to r.t. and stirred at that temperature for 20 h. It was then recooled to 0 °C and a solution of triethyl carbonate (86 μL, 0.71 mmol) in diethyl ether (1 mL) was added. Cooling was discontinued and the resulting solution was warmed up to reflux temperature over 48 h. NH_4Cl (sat. solution) (10 mL) was added and the solution concentrated. Dichloromethane (10 mL) was added and the phases separated. After extraction of the aqueous layer with two other portions of dichloromethane (2 × 10 mL), the organic phases were collected and evaporated to dryness under reduced pressure to afford an orange oil. On treatment with diethyl ether a precipitate appeared which was filtered and recrystallized from isopropyl alcohol to give the title compound as an orange-red solid (300 mg, 40%). m.p.: 135–140 °C (dec.). ^{1}H NMR ($CDCl_3$): 6.77 (d, *J* 16.5, 3H, CH=×3), 6.61 (d, *J* 16.5, 3H, CH=×3), 6.61 (s, 6H, Ar—H × 6), 4.44 (s, 6H, Fc—H × 6), 4.27 (s, 6H, Fc—H × 6), 4.15 (s, 15H, Cp × 3) and 3.56 (s, 18H, OMe × 6). ^{13}C NMR ($CDCl_3$): 158.6, 135.7, 126.6, 125.6, 125.5, 103.7, 83.6 (C, quat.), 69.1 (Cp), 68.8 (Fc—CH), 66.6 (Fc—CH) and 56.4 (OMe). UV–Vis ($CHCl_3$) $\lambda_{max}(\log\varepsilon)$ 452 nm (3.59). MS (ESI) *m*/*z* (%): 1054.8 ($[M+H-OH]^+$, 80%), 1053.7 ($[M-OH]^+$, 100). Calc. for $C_{61}H_{58}Fe_3O_7$: C, 68.43; H, 5.46. Found: C, 68.50; H, 5.44%.

3.11. Tris {4-[2-(E)-[4-(dimethylamino)phenyl]ethenyl]-2,6-(dimethoxy)phenyl}methanol (**6b**)

Prepared as above from **5b** (1.0 g, 3.5 mmol), *n*-butyllithium, (1.9 mL, 3.6 mmol; 1.88 M in methylcyclohexane), and diethyl carbonate (106 μL, 0.875 mmol) to give the title compound as a dark yellow solid after crystallization from diethyl ether (400 mg, 52%). m.p.: 165 °C (dec). ^{1}H NMR ($CDCl_3$): 7.40 (d, *J* 8.5, 6H, Ar—H × 6), 6.98 (d, *J* 16.0, 3H, CH=×3), 6.84 (d, *J* 16.0, 3H, CH=×3), 6.71 (d, *J* 8.5, 6H, Ar—H × 6), 6.64 (s, 6H, Ar—H × 6), 3.53 (s, 18H, OMe × 6) and 2.98 (s, 18H, NMe_2 × 3). ^{13}C NMR ($CDCl_3$): 158.6 (Ar—C, quat.), 149.8 (Ar—C, quat.), 135.9, 127.5, 127.3, 125.8, 124.8, 112.4, 103.9, 77.2, 56.3 (OMe × 2) and 40.41 (NMe_2). UV–Vis (CH_3CN) λ_{max}(log ε) 393 nm (3.81). MS (ESI) *m*/*z* (%): 860.0 ($[M+H-OH]^+$, 70%) and 858.9 ($[M-OH]^+$, 100). Calc. for $C_{55}H_{61}N_3O_7$: C, 75.40; H, 7.02; N, 4.80. Found: C, 75.37; H, 7.06; N, 4.72%.

3.12. Tris{2,6-dimethoxy-4-[2-(E)-(ferrocenyl)ethenyl]-phenyl}carbenium hexafluorophosphate (**7a**)

Hexafluorophosphoric acid (20 μl; 60% in water) was added to a suspension of carbinol **6a** (50 mg, 0.046 mmol) in ethanol (1 mL) at room temperature. The mixture became dark blue immediately. Diethyl ether was added (1 mL) followed by hexane (1 mL) and the suspension was filtered washed with hexane and dried under vacuum to give the title compound as dark blue solid (37 mg, 67%). ^{1}H NMR (CD_3CN): 7.40 (d, *J* 15.0, 3H, CH=×3), 6.66 (d, *J* 15.0, 3H, CH=×3), 6.61 (s, 6H, Ar—H × 6), 4.85 (s, 6H, Fc—H × 6), 4.72 (s, 6H, Fc—H × 6), 4.37 (s, 15H, Cp × 3) and 3.56 (s, 18H, OMe × 6). ^{13}C NMR (CD_3CN): 162.6 (Ar—C, quat.), 149.5 (Ar—C, quat.), 137.3 (CH), 126.8 (CH), 126.3 (Ar—C, quat.), 103.3 (CH), 73.7 (CH), 72.6.1 (CH), 70.0 (CH) and 56.9 (OMe). UV–Vis ($CHCl_3$) λ_{max}(log ε) 645 nm (4.35) and 900 nm (4.17). MS (ESI) *m*/*z* (%): 1054.8 ($[M+H-PF6]^+$, 80%) and 1053.7 ($[M-PF_6]^+$, 100). Calc. for $C_{61}H_{57}F_6Fe_3O_6P + H_2O$: C, 60.22; H, 4.89. Found: C, 60.55; H, 4.81%.

3.13. Tris{2,6-dimethoxy-4-[2-(E)-[4-(dimethylamino)-phenyl]ethenyl]phenyl}carbenium hexafluorophosphate (**7b**)

Prepared as above from hexafluorophosphoric acid (50 μl; 60% in water) and carbinol **6b** (100 mg, 0.11 mmol) to give the title compound as dark blue solid (100 mg,

90%). ^{1}H NMR (CD_3CN): 7.80 (d, *J* 8.5, 6H, Ar—H × 6), 7.63 (d, *J* 16.5, 3H, CH═×3), 7.52 (d, *J* 8.5, 6H, Ar—H × 6), 7.30 (d, *J* 16.5, 3H, CH═×3), 6.83 (s, 6H, Ar—H × 6), 3.62 (s, 18H, OMe × 6) and 3.23 (s, 18H, NMe_2 × 3). ^{13}C NMR (CD_3CN): 163.2 (Ar—C, quat.), 149.9 (Ar—C, quat.), 144.1 (Ar—C, quat.), 138.2 (Ar—C, quat.), 134.3 (CH), 130.5 (CH), 130.2 (CH), 126.1 (Ar—C, quat.), 121.4 (CH), 104.1 (CH), 57.2 (OMe × 2) and 47.6 (NMe_2). UV–Vis (CH_3CN) λ_{max}(log ε) 833 nm (4.54). MS (ESI) *m*/*z* (%): 859.8 ($[M+H-PF6]^+$, 60%) and 858.8 ($[M-PF_6]^+$, 100). Calc. for $C_{55}H_{60}F_6N_3O_6P + H_2O$: C, 64.63; H, 6.11; N, 4.11. Found: C, 64.81; H, 6.00; N, 4.05%.

3.14. Sample preparation for the pH dependent absorption measurements

Stock solutions for the dyes (2.50E-4 M to 4.10E-4 M see text) and TFA (51.9E-2 M or 1.29 M) were prepared in $CHCl_3$. The dye solutions were prepared by mixing 1 or 2 mL of the dye base solution with varying amounts of the TFA solutions or with varying amounts of neat TFA and the final volumes adjusted to 5 or 10 mL with $CHCl_3$.

Acknowledgements

A Marie Curie Intra-European Individual Fellowship to C.V.-B. (contract No. MEIF-CT-2003-501082) and an ENTER programme grant from the General Secretariat for Research for Technology to V.K. are gratefully acknowledged.

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