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Tris[4-(ferrocenylvinyl)-3-methylphenyl]methylium tetrafluoroborate: a strongly absorbing organometallic near-IR dye

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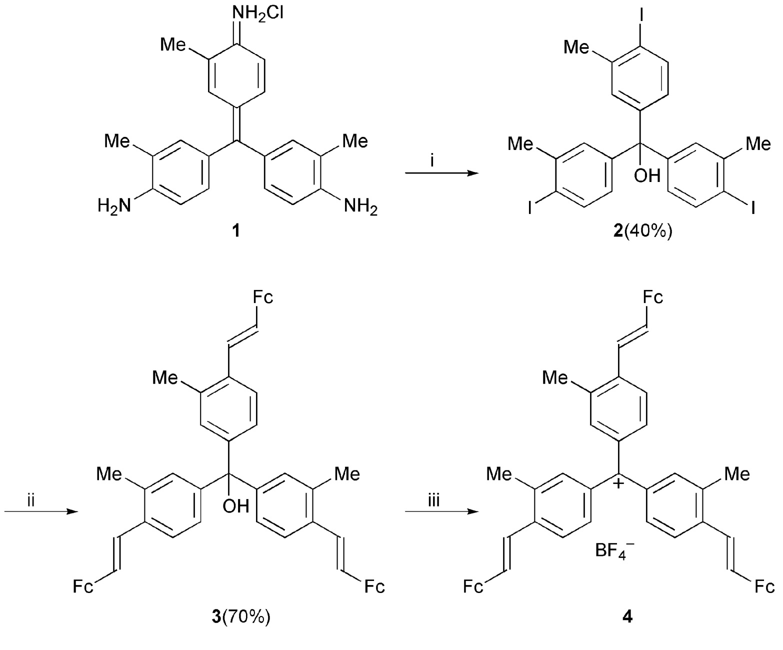
The trigonally symmetric tris[4-(ferrocenylvinyl)-3-methylphenyl]methylium ion 4, a π-conjugated metallocene analog of Crystal Violet, has been prepared and shows strong absorption in the near-infrared region (λ_{max} = 1068 nm).

Near-infrared (NIR) absorbing dyes are of current interest because of their potential applications in laser optical imaging systems, infrared photography and as biological stains.[1] They are usually prepared *via* end-capping of conjugated organic molecules with strong donor and acceptor substituents.[2] That ferrocene and some other metallocenes can act as strong donor groups,[3] leads to the prospect that acceptor substituted metallocenes may also produce NIR dyes. However, little progress has been made towards this end and apart from a few scattered reports of NIR absorbing ferrocene and ruthenocene derivatives attached to thioflavylium and tropylium ions (λ_{max} at *ca.* 800–900 nm),[4] little is known about metallocene based organometallic NIR dyes.

Acceptor substituted ferrocenes provide a tool for the synthesis of organometallic NIR dyes. Extended Hückel calculations have shown that, in these systems, an increase in the acceptor strength causes large bathochromic shifts due to considerable lowering of the already low-lying metal to ligand charge-transfer (MLCT) transitions.[5] At the same time, a more effective coupling between the MLCT and the ground state can also occur, resulting in an increased oscillator strength. We reasoned that, since carbocations are the strongest known acceptor groups, these effects would be maximized in systems where multiple ferrocene units are conjugatively linked to a carbocationic center. Such is the case with the tris[4-(ferrocenylvinyl)-3-methylphenyl]methylium tetrafluoroborate (**4**) whose synthesis and absorption properties are described in this communication.

Our synthesis started with the cheap, commercially available New Fuchsin (**1**) which *via* conventional hexazotization ($NaNO_2$, H_2SO_4) and the Sandmeyer reaction (KI, H_2O) was converted to the tris(iodo)aryl carbinol **2** in 40% overall yield (Scheme 1).[6] Threefold Heck reaction of **2** with vinyl ferrocene under Jefferey's conditions[7] produced the tris(ferrocenylvinyl)-aryl methanol **3** in 70% yield.[8] Protonation[9] of **3** with 42% HBF_4 in CH_2Cl_2 at room temperature then led to the quantitative formation of the cationic dye **4**. We have not yet been able to isolate **4**, since during aqueous work-up the dye quickly reverts to the carbinol **3**. However, once prepared, the dye solution is stable at room temperature over indefinite periods. The formation of **4** is clearly evident from ^{13}C NMR studies (Fig. 1). Thus, addition of 42% HBF_4 to a $CDCl_3$ solution of **3** leads to complete disappearance of the signal for the carbinol-carbon atom at 81.6 ppm with simultaneous appearance of a signal for the central cationic carbon of **4** at 181.3 ppm.[8] Moreover, in accordance to the known ^{13}C NMR studies on protonation of various trityl alcohols to the trityl cations,[9b] the ferrocenyl and the phenyl carbons of **3** underwent a large downfield shift ($\Delta\delta \approx 6$–12 ppm) on conversion to **4**.

The absorption spectrum of **4** (Fig. 2) showed two strong bands, one in the visible (λ_{max} = 625 nm, $\varepsilon = 6.16 \times 10^4$ M^{-1} cm^{-1}) and the other in the NIR region (λ_{max} = 1068 nm, $\varepsilon = 3.49 \times 10^4$ M^{-1} cm^{-1}). The latter values are more red-shifted than those of the known π-conjugated



Scheme 1 (i) $NaNO_2$, H_2SO_4, 0 °C then KI, H_2O, rt; (ii) vinyl ferrocene (4 equiv.), 30% $Pd(OAc)_2$, Bu_4NCl, KOAc, DMF, 80 °C; (iii) 42% HBF_4, CH_2Cl_2, rt.

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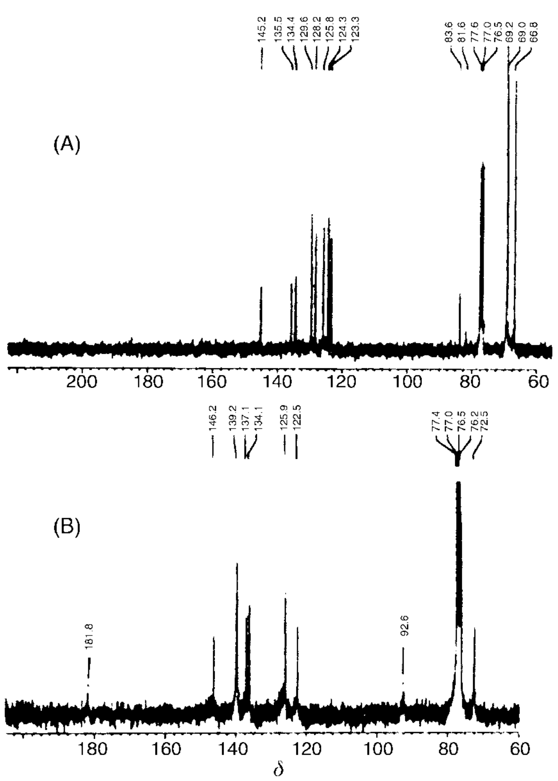


Fig. 1 Partial ^{13}C NMR spectra of **3** (spectrum A) and **4** (spectrum B).

triphenylmethane dyes (λ_{max} at *ca.* 705–830 nm).[10] In fact, the NIR band of **4**, both in its position and intensity of absorption, closely matches those of the longer wavelength absorbing cyanine and polymethine NIR dyes (λ_{max} 850–1100 nm).[1b,11] Such a large bathochromic shift is, presumably, caused by a lowering of the energy of the MLCT transitions in the cationic ferrocenyl styryl chromophore of **4** and the effect is further amplified as a consequence of its trigonal symmetry. The contribution of MLCT in inducing such a low-energy transition in **4** is most evident when one compares its absorption data with those reported for the structurally analogous organic cationic dyes **5a,b**.[12] Despite the fact that the donor capacity of ferrocene is comparable to that of the *p*-anisyl group[5b] and is perhaps, weaker than *N*,*N*-dialkylanilines, the latter dyes (**5a,b**), being devoid of any MLCT transitions, showed λ_{max} values at 608 nm ($\varepsilon = 3.38 \times 10^4$ M^{-1} cm^{-1}) and 684 nm ($\varepsilon = 0.68 \times 10^4$ M^{-1} cm^{-1}),[12,13] respectively, which are significantly blue-shifted from the lower energy band of **4**.

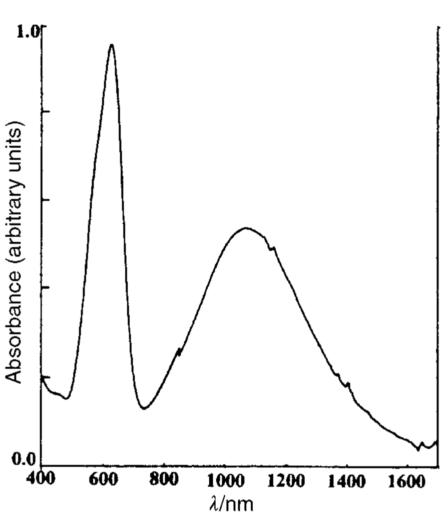
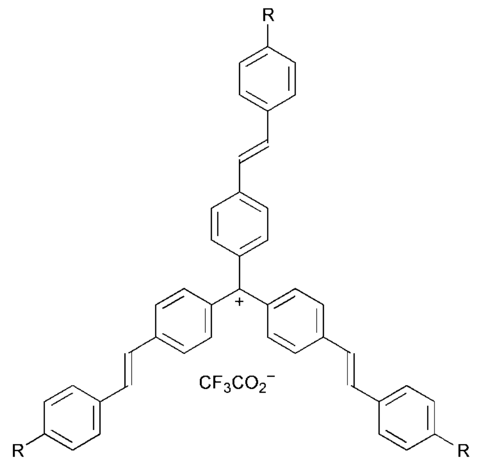


Fig. 2 Electronic spectrum of **4** (1.55×10^{-5} M in CH_2Cl_2/HBF_4).



5a R = NMe_2
5b R = OMe

It may be further noted that although NR_2 groups are widely used auxochromes in dye chemistry, increasing their number in triphenylmethane dyes leads to a gradual decrease in their λ_{max} values.[14] In contrast, we have shown that the presence of multiple ferrocene units in triphenylmethane dyes provides large bathochromic as well as hyperchromic effects which can be used to good advantage in the synthesis of new NIR dyes.

In conclusion, we have shown that multiple ferrocene units when conjugatively linked to a carbocation in a symmetric fashion, produce organometallic NIR dyes with strong absorptions. Based on these design elements, syntheses of other organometallic NIR dyes are currently being investigated.

Acknowledgements

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Notes and references

1 (*a*) M. Matsuoka, *Infrared Absorbing Dyes*, Plenum Press, New York, 1990; (*b*) J. Fabian, H. Nakazumi and M. Matsuoka, *Chem. Rev.*, 1992, **92**, 1197; (*c*) C. T. Chen and S. R. Marder, *Adv. Mater.*, 1995, **7**, 1030.

2 The same concept is used to prepare organic nonlinear optical chromophores: (*a*) *Nonlinear Optics of Organic Molecules and Polymers*, ed. H. S. Nalwa and M. Miyata, CRC Press, Boca Raton, 1997; (*b*) N. J. Long, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 21.

3 W. E. Watts, in *Comprehensive Organometallic Chemistry*, ed. G. Wilkinson, F. G. A. Stone and E. W. Abel, Pergamon Press, Oxford, 1982, vol. 8, p. 1051.

4 (*a*) W. M. Laidlaw and R. G. Denning, *J. Chem. Soc., Dalton Trans.*, 1994, 1987; (*b*) L. M. Tolbert, X. Zhao, Y. Ding and L. A. Bottomley, *J. Am. Chem. Soc.*, 1995, **117**, 12891; (*c*) V. Alain, A. Fort, M. Barzoukas, C. T. Chen, M. Blanchard-Desce, S. R. Marder and J. W. Perry, *Inorg. Chim. Acta*, 1996, **242**, 43; (*d*) A.-C. Ribou, J. P. Launay, M. L. Sachtleben, H. Li and C. W. Spangler, *Inorg. Chem.*, 1996, **35**, 3735; (*e*) J. Heck, H. C. Brussard, S. Dabek, T. Meyer-Friedrichsen and H. Wong, *Proc. SPIE*, 1997, **3147**, 53; (*f*) B. Bildstein, M. Schweiger, H. Kopacka, K. H. Ongania and K. Wurst, *Organometallics*, 1998, **17**, 2414; (*g*) I.-Y. Wu, J. T. Lin and Y. S. Wen, *Organometallics*, 1999, **18**, 320; (*h*) for electrochromic organometallic near-IR dyes, see N. C. Harden, E. R. Humphrey, J. C. Jefferey, S.-M. Lee, M. Marcaccio, J. A. McCleverty, L. H. Rees and M. D. Ward, *J. Chem. Soc., Dalton Trans.*, 1999, 2417 and references cited therein.

5 (*a*) M. L. H. Green, S. R. Marder, M. E. Thompson, J. A. Bundy, D. Bloor, P. V. Kolinsky and R. J. Jones, *Nature*, 1987, **330**, 360; (*b*) J. C. Calabrese, L.-T. Cheng, J. C. Green, S. R. Marder and W. Tam, *J. Am. Chem. Soc.*, 1991, **113**, 7227; (*c*) H. E. Bunting, M. L. H. Green, S. R. Marder, M. E. Thompson, D. Bloor, P. V. Kolinsky and P. V. Jones, *Polyhedron*, 1992, **11**, 1489.

6 S. Sengupta and S. K. Sadhukhan, *Tetrahedron Lett.*, 1999, **40**, 9157. **2**: mp 98–99 °C; δ_H (300 MHz, $CDCl_3$, *J*/Hz): 2.40 (9 H, s),

6.72 (2 H, dd, *J* 8.4, 2.1), 7.18 (3 H, d, *J* 2.1), 7.74 (3 H, d, *J* 8.4); δ_C (75 MHz, $CDCl_3$): 28.2, 81.0, 100.3, 126.9, 128.9, 138.5, 141.2, 146.2.

7 (*a*) B. Konig, H. Zeig, P. Bubenitschek and P. G. Jones, *Chem. Ber.*, 1994, **127**, 1811; (*b*) T. Jefferey, *Tetrahedron*, 1996, **52**, 10113.

8 **3**: mp 145–146 °C; δ_H (300 MHz, $CDCl_3$, *J*/Hz): 2.35 (9 H, s), 4.13 (15 H, s), 4.27 (6 H, br s), 4.46 (6 H, br s), 6.76 (3 H, d, *J* 16), 6.90 (3 H, d, *J* 16), 7.08 (3 H, dd, *J* 8.1, 1.4), 7.17 (3 H, d, *J* 1.4), 7.48 (3 H, d, *J* 8.1); δ_C (75 MHz, $CDCl_3$): 20.2, 66.8, 69.0, 69.2, 81.6, 83.6, 123.3, 124.3, 125.8, 128.2, 129.6, 134.4, 135.7, 145.2. **4**: δ_C (75 MHz, $CDCl_3$–42% HBF_4): 19.7, 72.5, 76.2, 92.6, 122.5, 125.9, 136.1, 137.1, 139.6, 139.7, 139.9, 146.2, 181.3.

9 (*a*) D. Hellwinkel, H. Stahl and H. G. Gaa, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 794; (*b*) B. Abarca, G. Asensio, R. Ballesteros and T. Varca, *J. Org. Chem.*, 1991, **56**, 3224.

10 (*a*) H. Schmidt and R. Wizinger, *Liebigs Ann. Chem.*, 1959, **623**, 204; (*b*) S. Akiyama, S. Nakatsuji, K. Nakashima, M. Watanabe and H. Nakazami, *J. Chem. Soc., Perkin Trans. 1*, 1988, 3155 and references cited therein.

11 (*a*) W. B. Tuemmler and B. S. Wildi, *J. Am. Chem. Soc.*, 1958, **80**, 3772; (*b*) F. M. Hamer, in *Chemistry of Heterocyclic Compounds*, Wiley Interscience, New York, 1964, vol. 18; (*c*) M. Zollinger, *Colour Chemistry. Synthesis, Properties and Applications of Organic Dyes and Pigments*, VCH, Weinheim, 1987.

12 C. Arbez-Gindre, C. G. Screttas, C. Fiorini, C. Schmidt and J. M. Nunzi, *Tetrahedron Lett.*, 1999, **40**, 7413.

13 The absorption spectrum of **5a** shows a pH dependent behavior. Unpublished work from these laboratories.

14 G. N. Lewis and M. Calvin, *Chem. Rev.*, 1939, **25**, 273.