Synthesis of Donor–Acceptor Substituted Molecular Caltrops: Strategic Use of an AB_3 Synthon Based on a Tetraphenylmethane Core

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Abstract: Using a tetraphenylmethane based AB_3 tecton, a facile synthetic route to donor-acceptor substituted unsymmetrical molecular caltrops is described. The former compound was readily prepared in two steps from the cheap commercial dye New Fuchsin.

Key words: molecular caltrops, dyad, tetraphenylmethane, Sonogashira coupling, Heck reaction

Photoinduced electron transfer (PET) plays a key role in natural photosynthesis.[1] In order to understand this process at a molecular level, many covalently bound donor-acceptor dyads have been investigated in recent years.[2,3] The efficiency of PET reaction in these dyads was found to be highly dependent on the distance and angles between the donor and the acceptor chromophores. In order to control these elements, a variety of spacer units, differing in length and/or topology, have been used between the donor and the acceptor units. It has been shown that dyads having flexible matrices can create problems in PET reactions. Due to their conformational freedom, such dyads can give rise to undesired associative interactions such as excimer formation, self-quenching, etc., which may severely interfere with the PET reaction. These problems can be minimized if a conformationally rigid spacer is used between the donor and the acceptor chromophores. We therefore undertook a program on the synthesis and PET reaction studies of a series of topologically rigid donor-acceptor dyads and in this paper, describe a facile synthetic route to unsymmetrical caltrop-shaped dyads **1** (Figure 1) in which the donor and the acceptor units are held in a rigid tetrahedral arrangement.

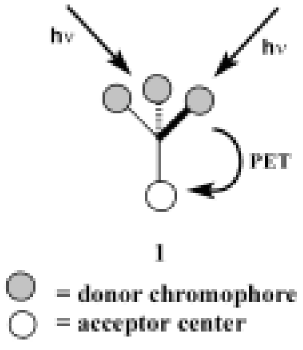
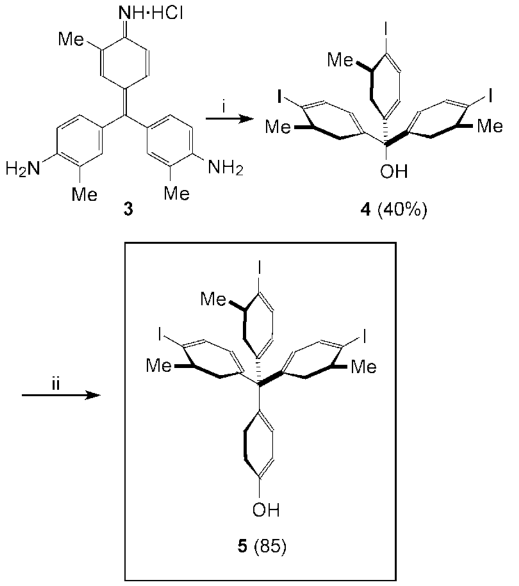


Figure 1

Symmetrical molecular caltrops such as **2** (Figure 1) have been the focus of many recent studies.[4] They are potentially useful in atomic force microscopy, photovoltaic cells, as the emitting layer in organic light emitting diodes (OLEDs) and in the preparation of dendritic light harvesting antennae and star-shaped multiredox systems. Rigid tetrahedral scaffolds such as tetraphenylmethane and to a lesser extent, 1,3,5,7-tetraphenyl adamantane (extended tetrahedron) are used for their synthesis.[5] On the other hand, synthesis of unsymmetrical molecular caltrops viz. **1** has received little attention.[6] The reported synthetic procedures are either target specific or involve cumbersome synthetic steps and therefore, lack a general synthetic appeal. The absence of a readily available centrally tetrahedral AB_3 synthon appears to be the major hurdle towards this end. In continuation of our interest in tetraphenylmethane based novel molecular architectures,[7] we now describe a general synthetic route to unsymmetrical molecular caltrops via the key use of a tetraphenylmethane based AB_3 tecton **5**.

Our synthesis started with the cheap commercial dye New Fuchsin **3** which via threefold diazotization ($NaNO_2$, dilute H_2SO_4, 0 °C) and iododediazoniation reaction (KI, H_2O, r.t.) produced the triiodoaryl carbinol **4** (40%) as described before (Scheme 1).[8] Acid catalyzed reaction of **4**



Scheme 1 Reagents and conditions: (i) dilute H_2SO_4, $NaNO_2$, 0 °C then KI, H_2O, r.t.; (ii) phenol (4 equiv), concd H_2SO_4, 80 °C.

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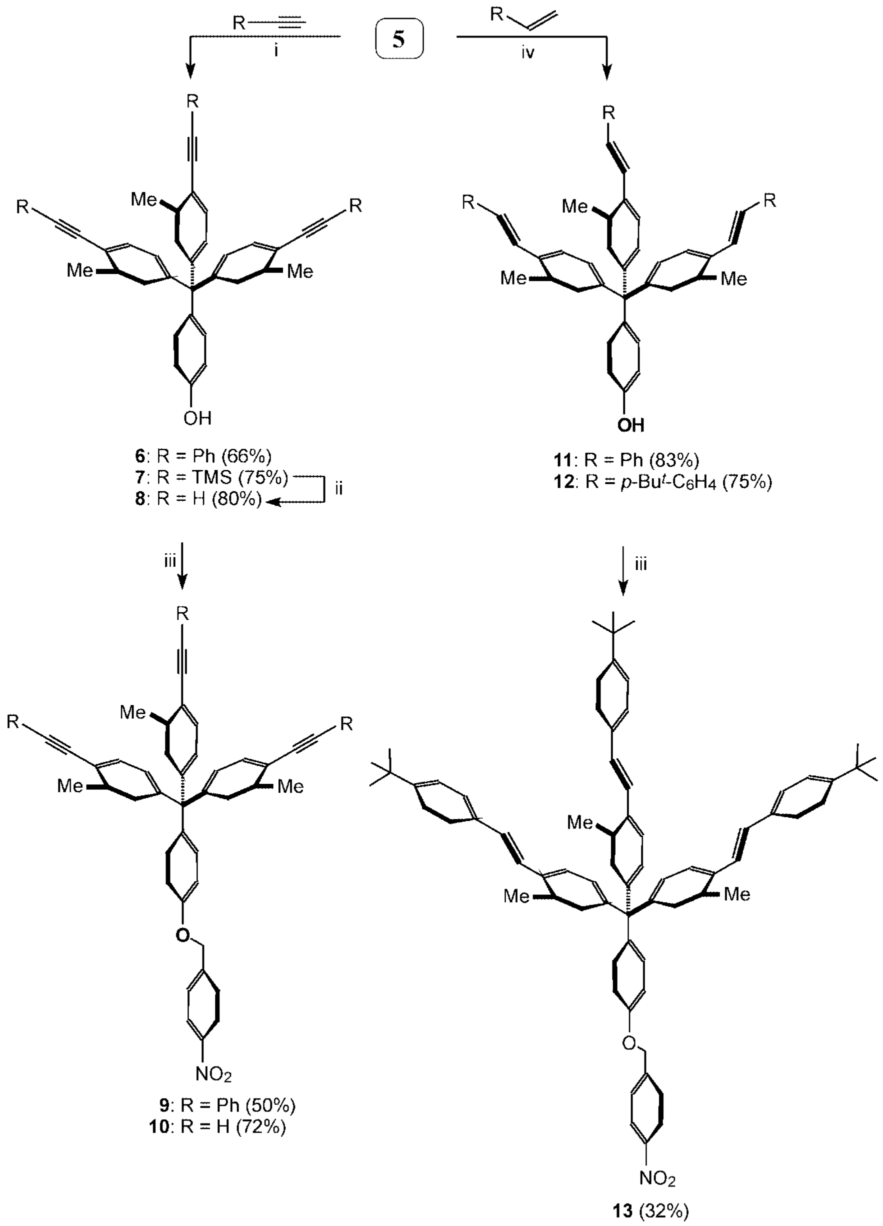
with excess phenol at 80 °C then led to **5**, the key AB_3 tecton, in 85% yield.[9] The *para*-isomer was obtained exclusively in this Friedel–Crafts type reaction. Towards synthesis of unsymmetrical molecular caltrops, we envisaged that three donor chromophores could be introduced into **5** via threefold Sonogashira or Heck reaction on the iodoaryl tripod. The acceptor chromophore could be subsequently introduced via the phenolic end. Since the Pd-catalyzed reactions would lead to either sp- or sp^2 hybridized linkers, it was expected that the topological rigidity of the tripod would remain unaffected.

We first investigated the threefold Sonogashira reactions on **5** using phenyl acetylene and TMS-acetylene [10% $PdCl_2(PPh_3)_2$, 10% CuI, Et_3N, DMF, r.t.][10] which gave rise to the tris-alkynylated products **6** (66%) and **7** (75%), respectively (Scheme 2).[11] The TMS-groups from **7** were then removed (NaOH, THF, r.t.) to give the terminally free tris-acetylene product **8** (80%). The latter may be further engaged in Pd-catalyzed couplings with aryl halides and triflates. However, attempted Sonogashira reaction of **5** with ethyl propiolate failed to give the desired coupling product. Instead, we obtained the product of the Michael addition of the phenol to the activated triple bond. The phenolic group in **6** and **8** were then reacted with *para*-nitrobenzyl bromide (K_2CO_3, CH_3CN, reflux) to produce the donor-acceptor substituted unsymmetrical caltrops **9** and **10** in good yields.[12] Here, the choice of nitrobenzene as the acceptor stemmed from two major considerations: firstly, nitrobenzene is an excellent electron acceptor ($E_{\text{A/A}^-}$ ♠ –1.2 eV) and secondly, its absorption maxima (a strong K-Band at 250–270 nm and a weak R-band at 300–320 nm) lie in the shorter wavelength side which



Scheme 2 Reagents and conditions: (i) 10% $PdCl_2(PPh_3)_2$, 5% CuI, Et_3N, DMF, r.t.; (ii) NaOH, THF, r.t.; (iii) *para*-nitrobenzyl bromide, K_2CO_3, CH_3CN, reflux; (iv) 10% $Pd(OAc)_2$, Bu_4NBr, KOAc, DMF, 100 °C.

would interfere least with the absorption bands from the tolan or stilbenoid donors. For example, the absorption spectrum of **9** in $CHCl_3$ showed strong absorptions at 295 nm (λ_{max}) and 315 nm with shoulders at 280 and 305 nm. The strong bands are due to the tolan donors (absorption maxima of **6**: λ_{max} 294 nm and 314 nm) and are distinctly different from the shoulders due to the nitrobenzene acceptor. Moreover, the band positions of the individual donor and acceptor units remained unaltered in **9** indicating that there are no ground state interactions between the two types of chromophores in the dyad. This was much expected since in a molecular caltrop (**1** or **2**), the central sp^3-hybridized carbon would disrupt any conjugation whatsoever between the attached chromophores.

In order to introduce stilbenoid donors, a threefold Heck reaction of **5** was carried out with styrene under Jeffery's PTC- conditions [cat. $Pd(OAc)_2$, Bu_4NBr, KOAc, DMF, 100 °C)][13] which led to the tristilbenoid phenol **11** in 83% yield (Scheme 2).[14] However, **11** was found to be sparingly soluble in common organic solvents. This solubility problem was solved by using *para*-*tert*-butyl styrene for the Heck reaction which produced the soluble tristilbenyl donor **12** in 75% yield.[14] The latter was then coupled with *para*-nitrobenzyl bromide, as before (K_2CO_3, CH_3CN, reflux), to produce the stilbene-nitrobenzene molecular caltrop **13** (32%) as a pale yellow solid.[12] The low yield of **13** was due to its poor solubility in the reaction medium which led to incomplete conversion. The absorption spectrum of **13** in $CHCl_3$ showed a broad maximum at 320 nm with a shoulder at 328 nm. The former was due to the stilbenoid donors (absorption maxima of **12**: 318 nm) and was slightly red shifted from that of *trans*-stilbene itself.[15] Presumably, a small degree of homoconjugation is present in **12** and **13** which operates through their central sp^3-hybridized carbons.[4d,e,7d] The shoulder at 328 nm was due to the R-band of the nitrobenzene acceptor. Again, no ground state interaction between the stilbene and the nitrobenzene chromophores was evident in **13**.

In conclusion, a facile synthetic route to (donor-acceptor substituted) unsymmetrical molecular caltrops is described via the key intermediacy of a centrally tetrahedral AB_3 tecton **5**. Further use of **5** in the synthesis of unsymmetrical caltrops can be envisaged via threefold Pd-catalyzed couplings on the iodoaryl tripod, conversion of the phenol to a triflate and further Pd-catalyzed reactions at the latter end.

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(9) **Compound 5**: mp 206–207 °C (MeOH). IR (KBr): 3400, 1605, 1500, 1460, 1370 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$/TMS): $\delta = 2.33$ (s, 9 H), 6.65 (dd, $J = 8.4$, 2.1 Hz, 3 H), 6.70 (d, $J = 6.6$ Hz, 2 H), 6.99 (d, $J = 6.6$ Hz, 2 H), 7.02 (d, $J = 2.1$ Hz, 3 H), 7.65 (d, $J = 8.4$ Hz, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 28.2$, 63.3, 98.7, 114.5, 130.1, 131.9, 138.0, 140.5, 146.5, 153.6.

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(11) Representative Procedure for Three-fold Sonogashira Couplings on **5**: $PdCl_2(PPh_3)_2$ (5 mg) was added to a degassed solution of **5** (0.10 g, 0.13 mmol), phenyl acetylene (0.08 g, 0.8 mmol) and CuI (4 mg) in a mixture of DMF (3 mL) and Et_3N (2 mL). The reaction mixture was stirred at r.t. for 16 h. It was then concentratedd under reduced pressure, diluted with water and extracted with CH_2Cl_2. The organic layer was dried and the solvent removed under reduced pressure. The residue was purified by silica gel chromatography (10% EtOAc in light petroleum) to give **6** (0.057 g, 66%) as a white solid; mp 126–127 °C ($CHCl_3$–MeOH). IR (KBr): 3410, 1600, 1520, 1465, 1360 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$/TMS): $\delta = 2.43$ (s, 9 H), 6.73 (d, $J = 8.6$ Hz, 2 H), 6.90–7.16 (m, 8 H), 7.29–7.48 (m, 12 H), 7.49–7.62 (m, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 21.0$, 64.5, 88.5, 93.8, 114.5, 121.2, 123.9, 125.6, 128.3, 128.7, 128.9, 130.1, 131.9, 132.2, 138.0, 139.5, 147.0, 156.5. **8**: mp 105–106 °C (MeOH). IR (KBr): 3290, 3000, 2910, 2090, 1595, 1480 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$/TMS): $\delta = 2.35$ (s, 9 H), 3.26 (s, 3 H), 6.71 (d, $J = 8.7$ Hz, 2 H), 6.93 (d, $J = 8$ Hz, 3 H), 7.00 (d, $J = 8.7$ Hz, 2 H), 7.01 (s, 3 H), 7.33 (d, $J = 8$ Hz, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 20.9$, 64.0, 80.9, 82.3, 114.5, 119.6, 128.3, 131.7, 132.1, 138.0, 139.9, 147.0, 153.7.

(12) **Compound 9**: mp 130–132 °C (MeOH). IR (KBr): 2916, 1596, 1521, 1500, 1442, 1344 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$/TMS): $\delta = 2.36$ (s, 9 H), 5.08 (s, 2 H), 6.78 (d, $J = 9$ Hz, 2 H), 6.92 (dd, $J = 8.1$, 2 Hz, 3 H), 7.01 (d, $J = 2$ Hz, 3 H), 7.06 (d, $J = 9$ Hz, 2 H), 7.25–7.33 (m, 11 H), 7.42–7.46 (m, 6 H), 7.54 (d, $J = 8.1$ Hz, 3 H), 8.18 (d, $J = 9$ Hz, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 21.4$, 64.5, 69.1, 88.5, 93.8, 114.2, 121.2, 123.9, 124.2, 128.0, 128.5, 128.7, 128.9, 131.3, 131.4, 131.9, 132.2, 132.6, 139.5, 139.8, 144.8, 147.0, 156.7.

Compound 10: mp 132–135 °C (MeOH). IR (KBr): 2900, 2100, 1590, 1518, 1487, 1350 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$/TMS): $\delta = 2.36$ (s, 9 H), 3.24 (s, 3 H), 5.09 (s, 2 H), 6.73 (d, $J = 9$ Hz, 2 H), 6.91 (dd, $J = 8$, 1.8 Hz, 3 H), 7.00 (d, $J = 1.8$ Hz, 3 H), 7.06 (d, $J = 9$ Hz, 2 H), 7.30–7.36 (m, 5 H), 8.08 (d, $J = 8.7$ Hz, 2 H).

Compound 13: mp 203–205 °C. IR (KBr): 2902, 1604, 1521, 1508, 1456, 1344, 1242 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$/TMS): $\delta = 1.33$ (s, 27 H), 2.36 (s, 9 H), 5.16 (s, 2 H), 6.87 (d, $J = 9$ Hz, 2 H), 7.00 (d, $J = 16.2$ Hz, 3 H), 7.05–7.12 (m, 6 H), 7.24 (d, $J = 9$ Hz, 2 H), 7.28 (d, $J = 16.2$ Hz, 3 H), 7.35–7.53 (m, 14 H), 7.62 (d, $J = 9$ Hz, 3 H), 8.25 (d, $J = 9$ Hz, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 20.7$, 31.7, 35.0, 64.1, 69.0, 114.0, 124.2, 124.4, 124.8, 125.8, 126.0, 126.6, 128.0, 129.5, 129.9, 130.3, 132.6, 133.1, 134.4, 135.1, 135.4, 140.5, 145.0, 146.4, 156.5.

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(14) **Compound 11**: mp 201–202 °C. IR (KBr): 3290, 1595, 1500, 1445, 1260 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$/TMS): $\delta = 2.35$ (s, 9 H), 6.73 (d, $J = 8.7$ Hz, 2 H), 7.00 (d, $J = 16.2$ Hz, 3 H), 7.05–7.11 (m, 6 H), 7.14 (d, $J = 8.7$ Hz, 2 H), 7.20–7.31 (m, 6 H), 7.34 (d, $J = 5.4$ Hz, 3 H), 7.35 (d, $J = 16.2$ Hz, 3 H), 7.45–7.54 (m, 9 H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 20.2$, 63.7, 114.3, 124.4, 126.1, 126.5, 127.4, 128.6, 129.1, 129.7, 132.2, 132.7, 133.7, 134.7, 137.8, 139.2, 146.3, 153.4.

Compound 12: mp 220–224 °C ($CHCl_3$–MeOH). IR (KBr): 3300, 1600, 1510, 1440, 1280 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.33$ (s, 27 H), 2.34 (s, 9 H), 4.67 (br s, 1 H), 6.72 (d, $J = 8.5$ Hz, 2 H), 6.98 (d, $J = 16$ Hz, 3 H), 7.04–7.11 (m, 6 H), 7.14 (d, $J = 8.3$ Hz, 2 H), 7.26 (d, $J = 16$ Hz, 3 H), 7.37 (d, $J = 8.2$ Hz, 6 H), 7.45 (d, $J = 8.8$ Hz, 6 H), 7.48 (d, $J = 9.2$ Hz, 3 H).

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