

Hexakis(2-pyridyl)- and hexakis(3-pyridyl)[3]radialene: novel, water-soluble [3]radialenes with potential utility for supramolecular chemistry

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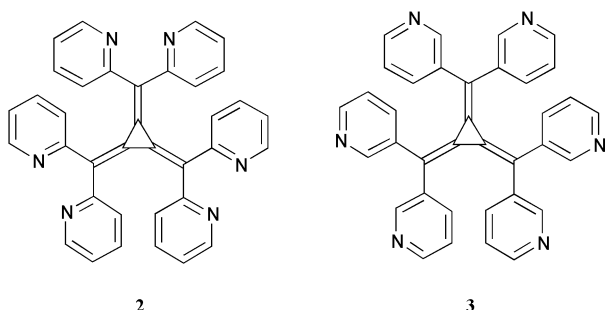
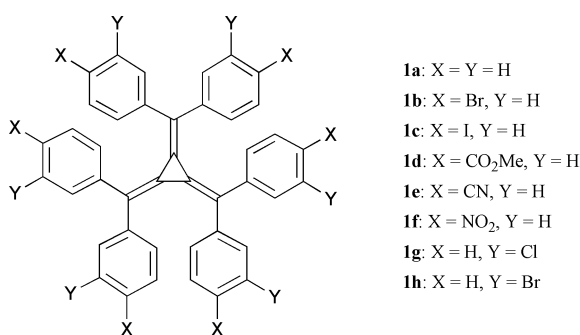
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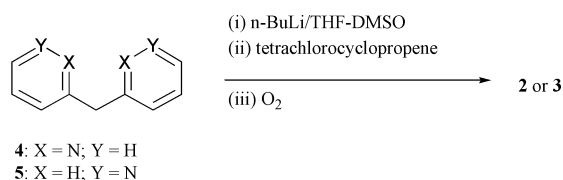
The titled [3]radialenes are the first, water-soluble hexaaryl[3]radialenes with considerably high electron affinity, their alkali metal reduction giving rise to anion-radicals and dianions stepwise as fairly stable species in degassed tetrahydrofuran.

Recently, we have reported the synthesis of hexaaryl[3]radialenes **1a–h**, revealing the importance of acidity of active methylene compounds for wider application of Fukunaga's hexacyano[3]radialene synthesis from tetrachlorocyclopropene and malononitrile.^{1,2} Although these molecules are not coplanar taking a propeller conformation, the quasi C_3 symmetric structures would provide versatile building blocks for either novel extended π -conjugated systems or supramolecular systems. In this context and in view of recent stimulative development of metallosupramolecular chemistry based on a variety of organic ligands and transition metal complexes,³ hexapyridyl[3]radialenes and related hexaheteroaryl[3]radialenes would be molecules of great interest. Here we report on the synthesis, electrochemical properties, and alkali metal reduction of hexakis(2-pyridyl)[3]radialene **2** and hexakis(3-pyridyl)[3]radialene **3**.



Radialenes **2**⁺ and **3**⁺ were synthesised, according to our standard procedure for hexaaryl[3]radialenes, by the reaction of tetrachlorocyclopropene with the carbanion of bis(2-pyridyl)methane **4**⁺ or bis(3-pyridyl)methane **5**⁺ in 51% and 39% yield, respectively, as stable crystalline orange substances (Scheme 1).

Notably, by virtue of the hydrogen-bonding ability of the sp² nitrogens, these radialenes, in particular **2**, are the first water-soluble hexaaryl[3]radialenes (water solubility; **2**: 17 mg mL⁻¹;



Scheme 1

3: 0.3 mg mL⁻¹). Regarding solubility, methanol, acetone, chloroform and dichloromethane are also good solvents but benzene, THF and ethyl acetate are poor solvents for these compounds.

These radialenes exhibit similar UV-vis absorptions to hexaphenyl[3]radialene **1a** (467 nm in CH₂Cl₂) with small solvent effects in neutral and basic media (Table 1). In acidic media, however, while **2** shows an appreciable red-shift of 36 nm (λ_{max} 465 nm/H₂O vs. 501 nm/1 M HCl), **3** undergoes a slight blue-shift (λ_{max} 459 nm/H₂O vs. 452 nm/1 M HCl).

Because of the electron-deficient nature of pyridyl groups, **2** and **3** are electron-poor radialenes showing two reversible reduction waves at considerably low potentials, the former compound being slightly more easily reduced (Fig. 1 and Table 1; the species responsible for the small oxidation peak at about -0.7 V is as yet uncertain). Their reduction potentials occupy positions between those of hexakis(4-bromophenyl)[3]radia-

Table 1 The longest absorption maxima and reduction potentials^a (CV) of hexaaryl[3]radialenes

Compound	λ_{max} /nm (log) ^b	¹ E _{red} /V	² E _{red} /V
1b ^c	485 (4.64)	-1.29	-1.77
3	465 (4.48)	-1.17	-1.64
2	464 (4.53)	-1.15	-1.55
1d ^c	488 (4.70)	-1.03	-1.33
1e ^c	488 (4.65)	-0.86	-1.11

^a V vs. Ag/Ag⁺ (Fc/Fc⁺ = +0.16 V), 0.1M n-Bu₄NClO₄/DMF, sweep rate 100 mVs⁻¹, rt. ^b In CH₂Cl₂. ^c Ref. 2.

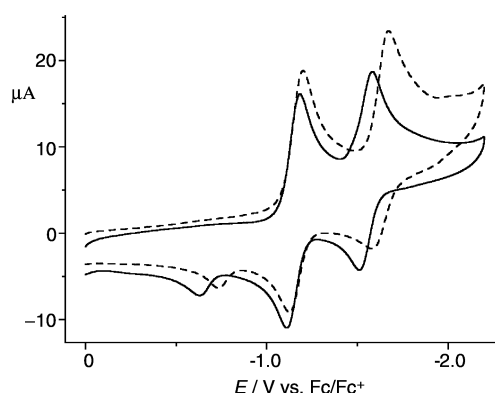
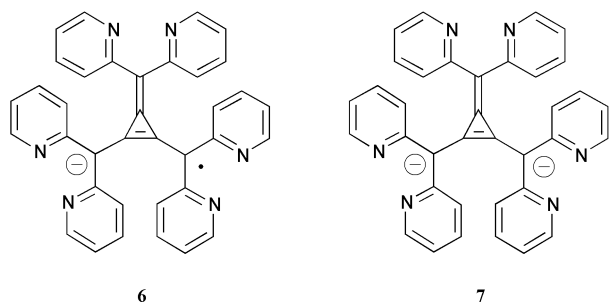


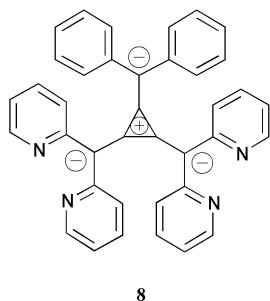
Fig. 1 Cyclic voltammograms of **2** (solid line) and **3** (broken line) at room temperature.

lene **1b** and hexakis(4-methoxycarbonylphenyl)[3]radialene **1d**.

Upon alkali metal reduction using 3% Na–Hg in degassed THF, radialene **2** at first exhibits new increasing absorptions at 325, 484 and 794 nm. The last near-infrared absorption decreases on further reduction, finally to show absorption maxima at 318 and 435 nm (Fig. 2). The solution on the way to the final spectrum exhibited a somewhat broad ESR signal (Fig. 3)⁶ and the final solution was ESR silent. These observations point to the intermediate and final formation of anion radical **6**



and dianion **7**, respectively, as considerably stable species. The ¹H NMR spectrum of dianion **7**[†] formed in CD₃CN under similar conditions shows the presence of two kinds of 2-pyridyl groups by exhibiting two sets of pyridyl protons in 1:2 integral ratio, indicating a C₂ structure **7** (dipyridylmethyl anion parts are probably twisted from the triafulvene framework) rather than a C₃ symmetric tripolar structure **8**. Upon exposure to air, the



solutions of both **6** and **7** rapidly regenerated **2**. In the synthesis of **1a–h**, we have assumed the intermediacy of dianions like **7** and it is the first one to be observed spectroscopically.²

Similar reduction of **3** exhibited new absorptions at 594 and 841 nm with decrease of a strong absorption at 466 nm;

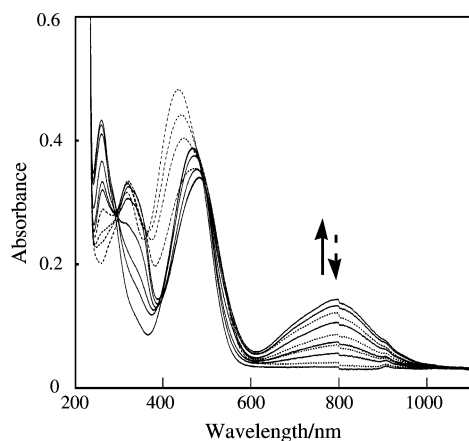


Fig. 2 UV-vis spectral change upon reduction of **2** with 3% Na–Hg in degassed THF (rt). Solid lines show increase of radical anion **6** and dotted lines decrease of **6** finally to form dianion **7**.

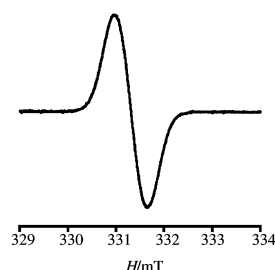


Fig. 3 ESR spectrum observed during 3% Na–Hg reduction of **2** in THF (anion radical **6**).

however, in this case the solubility of the resulting anion-radical salt was very low and it almost completely separated as a dark red solid from the solution, preventing further reduction to dianion in THF. The reduction of **3** in acetonitrile led to its dianion (λ_{\max} 441 nm).

There can be envisioned a good number of hexaheteroaryl[3]radialenes of structural and physicochemical interest other than **2** and **3**. The successful synthesis of **2** and **3** would promise the synthesis of those compounds and such attempts are in progress. We have also been attempting the preparation of metal complexes of **2** and **3** and have obtained several of these; however, attempts to obtain single crystals suitable for X-ray analysis have not yet met with success.⁷

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Notes and references

[†] Selected data for **2**: mp > 220 °C (decomp.); MS (EI) m/z 540 (M⁺); ¹H NMR (270 MHz, acetone-*d*₆) δ 8.07 (ddd, $J = 4.7, 2.0, 1.0$ Hz, 6H), 7.16 (dt, $J = 7.6, 2.0$ Hz, 6H), 7.09 (ddd, $J = 7.6, 4.7, 1.4$ Hz, 6H), 6.88 (ddd, $J = 7.6, 1.4, 1.0$ Hz, 6H); (500 MHz, CDCl₃) δ 8.31–8.27 (m, 6H), 7.06–7.01 (m, 12H), 6.95–6.91 (m, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 157.68, 148.74, 134.80, 126.60, 126.31, 121.97, 121.77; UV-vis (H₂O) λ_{\max} (log ϵ) 259 (4.49), 288sh (4.33), 340sh (3.89), 465 (4.54); (CH₂Cl₂) λ_{\max} (log ϵ) 259 (4.53), 290sh (4.31), 342sh (3.84), 464 (4.53); (1M HCl) λ_{\max} (log ϵ) 241sh (4.40), 264 (4.42), 302 (4.43), 364sh (4.01), 501 (4.52).**3**: mp > 240 °C (decomp.); MS (FAB) m/z 541 (M⁺+1); ¹H NMR (270 MHz, CDCl₃) δ 8.46 (dd, $J = 4.8, 1.6$ Hz, 6H), 7.98 (dd, $J = 2.3, 0.8$ Hz, 6H), 7.23 (ddd, $J = 7.8, 2.3, 1.6$ Hz, 6H), 6.97 (ddd, $J = 7.8, 4.8, 0.8$ Hz, 6H); ¹³C NMR (67.8 MHz, CDCl₃) δ 150.32, 148.84, 136.47, 135.33, 122.40, 119.22, 118.55; UV-Vis (H₂O) λ_{\max} (log ϵ) 264 (4.43), 459 (4.44); (CH₂Cl₂) λ_{\max} (log ϵ) 229 (4.46), 264 (4.50), 465 (4.48); (1M HCl) λ_{\max} (log ϵ) 232 (4.60), 266 (4.52), 452 (4.52).**7**: ¹H NMR (270 MHz, CD₃CN) δ 8.36 (d, $J = 5.0$ Hz, 2H), 8.00 (brs, 4H), 7.48 (m, 4H), 7.05 (m, 8H), 6.93 (m, 2H), 6.36 (m, 4H). The poor solubility of this dianion makes the measurement of ¹³C NMR difficult.

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- 4 A. J. Canty and N. J. Minchin, *Aust. J. Chem.*, 1986, **39**, 1063.
- 5 A. R. Katritzky, A. R. Lapucha, R. Murugan, F. J. Luxen, M. Siskin and B. Glen, *Energy Fuels*, 1990, **4**, 493; We prepared **5** in similar way to **4** (ref. 4).
- 6 The broadening of the signal might be due to slight separation of the radical-anion salt as solid from the solution.
- 7 Prof. P. J. Steel and co-worker have successfully obtained single crystals of a silver complex of **2** to reveal a hexanuclear silver array structure; see the accompanying paper (b109214f).