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Synthesis, properties, molecular structure and electron transfer salts of 13,13,14,14-tetracyano-1,6- and -1,8-pyrenoquinodimethanes (1,6-TCNP and 1,8-TCNP)

Ken-ichi Sugiura,[a] Shinji Mikami,[a] Kentaro Iwasaki,[b] Shojun Hino,[b] Eiji Asato[c] and Yoshiteru Sakata*[a]

[a]*The Institute of Scientific & Industrial Research (ISIR), Osaka University, 8-1 Mihogaoka, Ibaraki, Osaka, 567-0047, Japan. E-mail: sakata@sanken.osaka-u.ac.jp*
[b]*Faculty of Engineering, Chiba University, Inageku, Chiba, 263-8522, Japan*
[c]*Department of Chemistry, Biology and Marine Science, University of the Ryukyus, Nishihara-cho, Okinawa, 903-0213, Japan*

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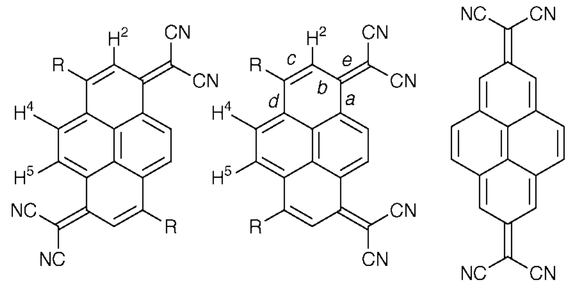
A guideline for a stable π-extended Wurster type redox system is proposed and two new acceptor molecules having a pyrene π-system were prepared and structurally characterised. 3,8-Bis(3′,5′-di-*tert*-butylphenyl)-13,13,14,14-tetracyano-1,6-pyrenoquinodimethane gave an electron transfer complex with Mn(TPP) ($H_2TPP = m$-tetraphenylporphyrin) containing a coordination bond.

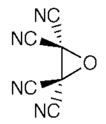
Introduction

Molecule-based electron transfer complexes have been attracting much attention in terms of their conductivity and magnetism over the last two decades.[1] Expansion of the π-electronic system of component molecules is one of the most important and promising approaches, not only to achieve high conductivity,[2] but also for attaining strong effective magnetic coupling.[3] During the last three decades, many new π-expanded redox systems based on Hünig's classification[4] have been reported.[2] However, when a redox active π-electron system is expanded, the thermodynamic and kinetic stability of the molecule is diminished.[5,6] Here, we wish to propose a guideline for the design of π-expanded redox systems and to report the synthesis of two new acceptor molecules, **1a** and **1b**, both of which contain a pyrene nucleus and also describe an electron transfer salt of **1a**.

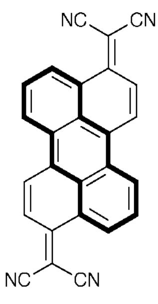


(1,6-TCNP) **1a** (1,8-TCNP) **1b** (2,7-TCNP) **1c**

R = 3′,5′-di-*tert*-butylphenyl (DTBuP)



TCNEO



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Results and discussion

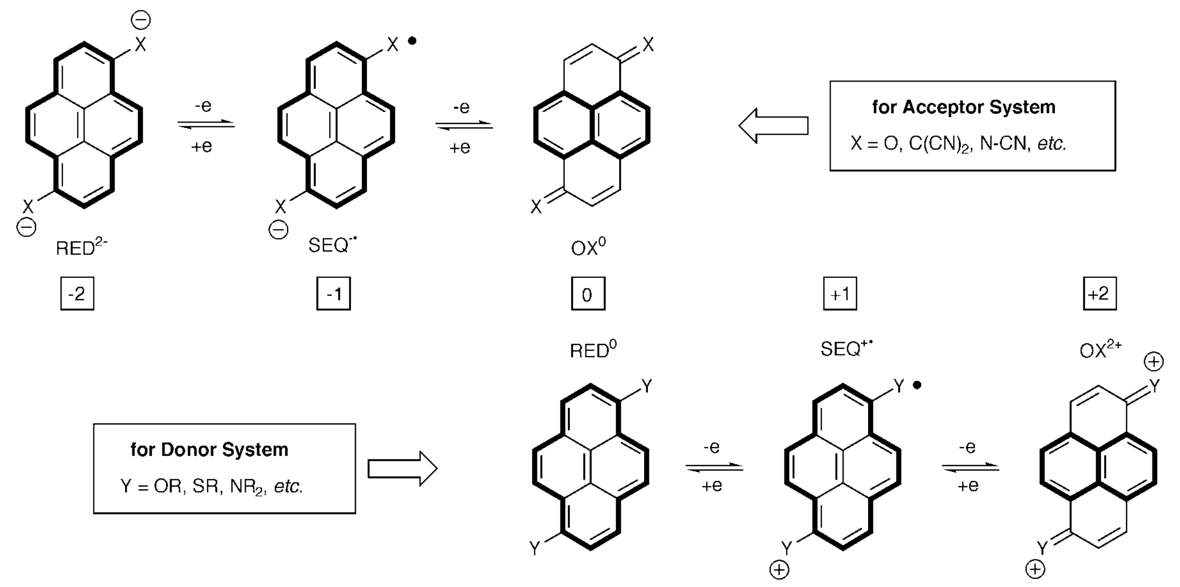
Molecular design

The molecular design was carried out based on the following considerations. *peri*-Condensed aromatic compounds containing –OR, –SR, $-NR_2$, =O, $=C(CN)_2$, and =N–CN substituents at the α-position act as *multi redox Wurster type molecules*[4] to give three stable redox states, *i.e.*, reduced state (RED), semiquinone state (SEQ) and oxidised state (OX), with an example based on the pyrene nucleus shown in Scheme 1.

The most striking feature in Scheme 1 is OX with a π-expanded quinonoid structure, which is stabilized by the central 10-electron naphthalene π-system. By contrast, substituents at β-positions do not provide stable OXs. Substituents having lone-pair electrons such as OR, SR[7] and NR_2[8,9] produce donor molecules under ambient conditions, whereas the introduction of exomethylenoid groups such as =O,[10,11] $=C(CN)_2$, or =N–CN produce acceptor molecules. This observation evolved from our previous study revealing that the introduction of $-NMe_2$ groups to α- but not β-positions of a pyrene molecule produces a stable redox system.[8,9] Based on this, we designed and synthesized two new acceptor molecules based on 13,13,14,14-tetracyano-1,6- and -1,8-pyrenoquinodimethane, **1a** (1,6-TCNP) and **1b** (1,8-TCNP) both of which have $=C(CN)_2$ groups at the α-positions of pyrene.[6] These molecules will be expected to act as *advanced acceptors* capable of not only accepting electrons but also bonding to transition metals similarly to tetracyanoethylene (TCNE).[12]

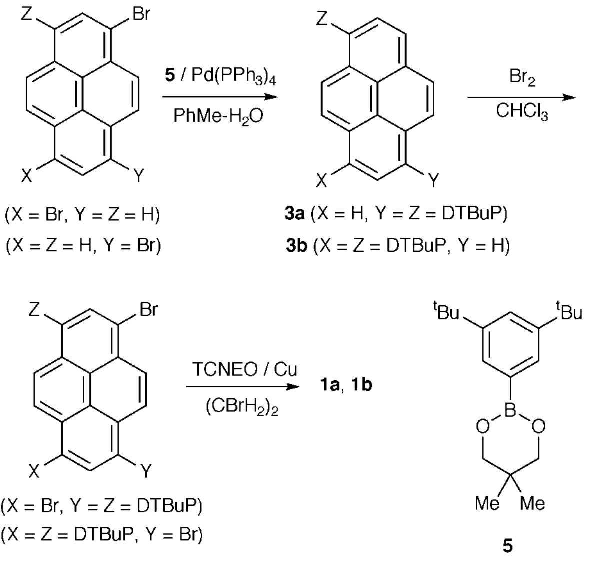
Preparation

The synthetic route to **1a** and **1b** is shown in Scheme 2. Although various methods are reported for the introduction of a dicyanomethylene unit,[13] we employed the most simple route using a dicyanocarbene intermediate generated from tetracyanoethylene oxide (TCNO).[14] However, the reaction of **2a**



Scheme 1 Three redox stages for π-extended Wurster-type redox molecules using pyrene. RED and SEQ states are stabilized by the aromaticity of pyrene; the OX state is stabilized by that of naphthalene.

and/or **2b**[15] with TCNEO gave sparingly soluble blue solids. To increase the solubility of the final product, 3′,5′-di-*tert*-butylphenyl (DTBuP) groups were introduced using an improved Suzuki coupling reaction.[16] Subsequent bromination of **3a** and **3b** gave **4a** and **4b**, respectively, which were refluxed with TCNEO in 1,2-dibromoethane to yield **1a** and **1b** quantitatively. In contrast to the instability of **1c**,[6] **1a** and **1b** are quite stable toward oxygen, water and heat, and can be kept for more than a year under ambient conditions.



Scheme 2

Spectroscopic studies

In electrochemical measurements (Table 1), two reversible reduction processes were observed for **1a** and **1b**. The reduction potentials are slightly lower than those of tetracyanoquinodimethane (TCNQ). The differences between the first and second reduction potentials (0.31 V for **1a** and 0.28 V for **1b**) are much smaller than the corresponding values of TCNQ and 11,11,12,12-tetracyano-2,6-naphthoquinodimethane (TNAP), and are comparable to that for 11,11,12,12-tetracyano-2,6-anthraquinodimethane (TANT) (0.32 V), reflecting the decrease of on-site coulomb repulsion by expansion of the π-systems.[17] Spectroscopic properties also support this result. In ^{1}H NMR spectra, the chemical shift of H^2 was observed at 7.62 and 7.59 ppm for **1a** and **1b**, respectively. Other protons, H^4 and H^5, were observed in the aromatic region. These results indicate that **1a** and **1b** are π-extended quinonoid molecules that are stabilized by naphthalene aromaticity.

Table 1 The first and second half-wave reduction potentials and the differences between these (Δ*E*) for **1** and related compounds

Compound	$E_1^{RED}{}_{1/2}$/V	$E_2^{RED}{}_{1/2}$/V	Δ*E*/V
1a[a]	+0.11	−0.20	0.31
1b[a]	+0.12	−0.16	0.28
1c[b,c]	+0.30	−0.01	0.31
TCNQ[a]	+0.25	−0.38	0.63
TNAP[a]	+0.27	−0.18	0.45
TANT[c,d]	+0.25	−0.07	0.32

[a] V *vs.* Ag/AgCl, Bu_4NPF_6 in PhCN. [b] From ref. 6(*c*). [c] The values are redefined in terms of the Ag/AgCl system. [d] From ref. 18(*b*).

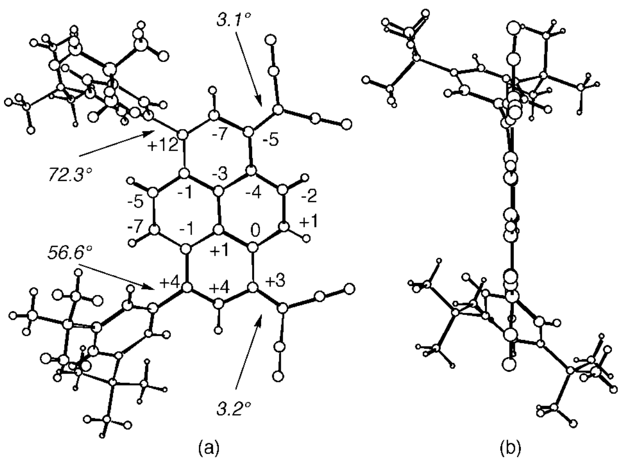


Fig. 1 Molecular structure of compound **1b**, (a) top view and (b) side view. Numbers refer to the deviation (in units of 0.01 Å) from the least squares plane defined by the 16 carbon atoms. Numbers in italics are the dihedral angles between the pyrene plane and dicyanomethylene moiety or DTBuP rings.

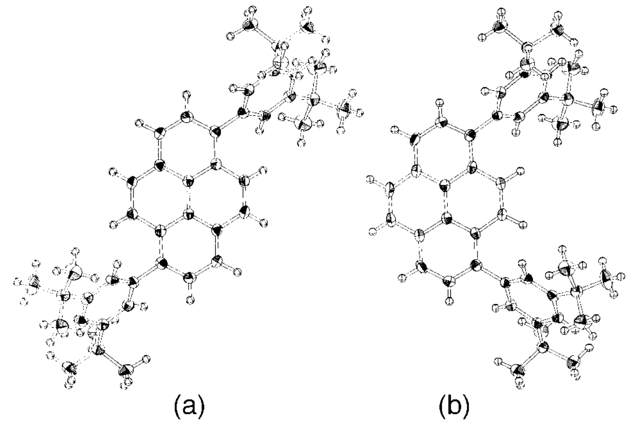


Fig. 2 Crystal structures of **3a** (a) and **3b** (b). Thermal ellipsoids are at the 50% probability level. The dihedral angles between the DTBuP groups and the pyrene nucleus are 56.1 and 54.7° for **3a** and **3b**, respectively.

Crystallographic studies

The X-ray structure of **1b** (Fig. 1) is shown along with reference compounds, **3a** and **3b** (Fig. 2). The dihedral angles between DTBuP groups and pyrene planes are 56.6 and 72.3° for **1b** *cf.* 56.1 and 54.7° for **3a** and **3b**, respectively. Although the bond distances for **3a** and **3b** are in the range for the reported unsubstituted pyrene,[18] the intramolecular bond lengths show characteristic bond alternation for the *peri*-condensed moiety; the following indicated a π-expanded quinonoid structure: *a*: 1.47 Å, *b*: 1.44 Å, *c*: 1.35 Å, *d*: 1.45 and *e*: 1.39 Å. Interestingly, the pyrene moiety is almost flat (within ±0.12 Å from the least squares plane), although steric repulsion between the interior CN group and *peri*-hydrogen is expected for **1b**. This planer structure is in marked contrast to the reported butterfly structures of benzo-annulated TCNQ derivatives,[19,20] *e.g.*, 11,11,12,12-tetracyano-1,4-naphthoquinodimethane (TCNaQ)[21] and 11,11,12,12-tetracyano-9,10-anthraquinodimethane (TCAQ).[22] The dihedral angle between the aromatic plane and dicyanomethylene moieties are only 3.2 and 3.1°.

Electron transfer complex formation reactions

To demonstrate the potential of 1,6- and 1,8-TCNP as advanced electron acceptor molecules, *i.e.*, capable of accepting electrons and bonding to metal cations, we performed complex formation reactions with [Mn^{II}(TPP)]·py (H_2TPP = *meso*-tetraphenylporphyrin, py = pyridine),[23] whose electron transfer complex with TCNE is known as a molecule-based ferrimagnet having a strong exchange interaction.[3d] The reaction between **1a** and [Mn^{II}(TPP)]·py gave **6** as a black powder. The following observations support the ionic nature of the complex: (1) significantly lower values of ν_{CN} stretching vibrations (2156m and 2068s cm^{-1}) compared with that of the neutral state **1a**;[24] (2) good agreement of an observed effective magnetic moment of **6** at room temperature (5.18 μ_B), with the calculated value for an independent isotropic system described by $g = 2$, $S = 2$ and $S = 1/2$ (5.20 μ_B);[25] and (3) a sharp absorption at $g = 2.002$, which is attributable to the π-anion radical and the unobserved Mn^{II} absorption in the EPR spectrum in the solid state. Furthermore, the core ionization potentials observed for Mn $2p_{3/2}$ and Mn $2p_{1/2}$ of **6** are much closer to those of six coordinate [Mn^{III}(TPP)][TCNE]·2PhMe than five coordinate [Mn^{III}(TPP)]Cl, indicating that **6**, like [Mn^{III}(TPP)][TCNE], is an ionic ground state electron transfer salt with a coordination bond (Table 2).

Conclusion

We have devised a strategy to prepare π-extended Wurster-type redox systems. In contrast to the instability of the β-substituted analogue **1c**, compounds **1a** and **1b** are stable in several oxidation states. Decreases of reduction potentials and small on-site coulomb repulsion for **1a** and **1b**, as compared with those for TCNQ, are attributable to the expansion of the π-electron system. This is in marked contrast to extended systems prepared by the benzo-annulation method, which is frequently used for expansion of redox π-systems.[19,20] In the benzo-annulation methodology the annulated butadiene unit, which perturbs with the parent π-system in a HOMO$^{\text{butadiene}}$–LUMO$^{\text{quinoid}}$ manner (a_2 symmetry) and a LUMO$^{\text{butadiene}}$–HOMO$^{\text{quinoid}}$ manner (b_2 symmetry), produces a molecule with only weak electron affinity.[26] Our present methodology can be widely used for the creation of new redox π-systems for advanced materials with elaborated physical properties.

An extension of our molecular design, *e.g.* to **7**, using the perylene system, should stabilize the OX state owing to the aromaticity of anthracene; it is also expected to be a π-extended redox system. We are currently working on this stage.

Experimental

General methods

Melting points were measured with a Yanako hot stage apparatus without correction. The ^{1}H and ^{13}C NMR spectra were recorded on a JEOL EX-270 (270 MHz and 67.5 MHz for ^{1}H and ^{13}C, respectively) spectrometer in $CDCl_3$ with TMS as the internal standard for ^{1}H and the solvent as the external standard for ^{13}C (77.0 MHz). Elemental analysis was performed using a Perkin-Elmer 2400 apparatus. FAB mass spectra were recorded on a JEOL JMS-600 spectrometer using 3-nitrobenzyl alcohol as a matrix. Absorption spectra were obtained with a Shimadzu UV-PC3100 spectrometer. Cyclic voltammetry was performed with a BAS CV-50 set-up using glassy carbon working, Pt counter and Ag/AgCl reference electrodes. The detailed conditions of the XPS measurements[27] and magnetic measurements[28] have been reported elsewhere.

1,6-Bis(3′,5′-di-*tert*-butylphenyl)pyrene 3a

A mixture of 3.00 g of **2a**,[15] 6.07 g of **5** (2.4 equiv.),[16] 1.00 g of freshly prepared $Pd(PPh_3)_4$,[29] 50 mL of aqueous 1 M K_2CO_3 and 50 mL of toluene was refluxed with vigorous stirring under nitrogen for 36 h. After cooling to room temperature, the organic layer was separated and extracted with three 50 mL portions of toluene. The organic phase was dried over Na_2SO_4 and the solvent was removed under reduced pressure. The dark

Table 2 XPS core ionization potentials (eV) for **6** and related compounds[a]

	Cl 2p	C 1s	N 1s	Mn 2p$_{3/2}$	Mn 2p$_{1/2}$
6		285.0	399.0	642.6	654.2
1a		284.7	398.5		
[Mn^{II}(TPP)]·py		284.9	398.4	641.1	653.1
[Mn^{III}(TPP)]Cl	197.6	284.9	398.9	642.2	653.8
[Mn^{III}(TPP)][TCNE]·2PhMe		284.9	399.1	642.6	654.2

[a] The spectrometers were calibrated such that the Au 4f$_{7/2}$ peak of the clean sputtered metals appeared at 84.0 eV. The ionization potentials are reproducible to a precision of ⩽ ±0.10 eV.

colored residue was chromatographed on SiO_2 eluting with hexane. Crystallization from heptane gave 4.07 g of **3a** (82%): mp 279.0–280.0 °C; ^{1}H NMR ($CDCl_3$, 270 MHz): $\delta=8.23$ (d, $J=9.2$ Hz, 2H), 8.20 (d, $J=7.6$ Hz, 2H), 8.04 (d, $J=9.2$ Hz, 2H), 8.02 (d, $J=7.6$ Hz, 2H), 7.55 (t, $J=1.6$ Hz, 2H), 7.49 (d, $J=1.6$ Hz, 4H), 1.44 (s, 36H); ^{13}C NMR ($CDCl_3$, 67.5 MHz): $\delta=150.8$, 140.0, 138.6, 132.2, 128.7, 128.4, 126.7, 126.0, 124.8, 121.6, 120.1, 35.1, 31.7; MS: *m/z* 579 (M + 1). Anal. Calc. for $C_{44}H_{50}$: C, 91.29; H, 8.71. Found: C, 91.04; H, 8.46%. This compound was structurally characterized [Fig. 2(a)].

1,8-Bis(3′,5′-di-*tert*-butylphenyl)pyrene 3b

A procedure similar to that described above was used for the synthesis of **3b** starting from 3.00 g of **2b**, 5.57 g of **5**, 1.00 g of $Pd(PPh_3)_4$, 50 mL of aqueous 1 M K_2CO_3 and 50 mL of toluene; this yielded 3.40 g of **3b** (70%): mp 196.0–197.0 °C (from heptane); ^{1}H NMR ($CDCl_3$, 270 MHz): $\delta=8.22$ (d, $J=7.9$ Hz, 2H), 8.17 (s, 2H), 8.10 (s, 2H), 8.03 (d, $J=7.9$ Hz, 2H), 7.52 (t, $J=1.6$ Hz, 2H), 7.48 (d, $J=1.6$ Hz, 4H), 1.40 (s, 36H); ^{13}C NMR ($CDCl_3$, 67.5 MHz): $\delta=150.5$, 140.1, 138.5, 130.7, 128.3, 127.7, 127.2, 125.4, 125.0, 124.6, 121.0, 35.1, 31.7; MS: *m/z* 579 (M + 1). Anal. Calc. for $C_{44}H_{50}$: C, 91.29; H, 8.71. Found: C, 91.07; H, 8.67%. This compound was structurally characterized [Fig. 2(b)].

1,6-Dibromo-3,8-bis(3′,5′-di-*tert*-butylphenyl)pyrene 4a

A solution containing 0.36 mL of Br_2 and 17 mL of $CHCl_3$ was added dropwise into a solution containing 2.0 g of **3a** and 17 mL of $CHCl_3$. After stirring for 10 h at room temperature, 15 mL of MeOH was added. The precipitated solid was collected and recrystallized from toluene–heptane (1 : 1) (2.15 g, 85%): mp > 300 °C; ^{1}H NMR ($CDCl_3$, 270 MHz): $\delta=8.41$ (d, $J=9.6$ Hz, 2H), 8.30 (s, 2H), 8.24 (d, $J=9.6$ Hz, 2H), 7.55 (t, $J=1.3$ Hz, 2H), 7.43 (d, $J=1.3$ Hz, 4H), 1.44 (s, 36H); ^{13}C NMR ($CDCl_3$, 67.5 MHz): $\delta=150.8$, 140.0, 138.6, 132.2, 128.6, 128.4, 126.0, 124.8, 121.6, 120.1, 35.1, 31.7; MS: *m/z* 737 (M^+). Anal. Calc. for $C_{44}H_{48}Br_2$: C, 71.74; H, 6.57; Br, 21.69. Found: C, 71.68; H, 6.43; Br, 21.90%.

1,8-Dibromo-3,6-bis(3′,5′-di-*tert*-butylphenyl)pyrene 4b

A procedure similar to that described above was used for the synthesis of **4b** starting from 3.00 g of **3b**, 1.66 g of Br_2 and 52 mL of $CHCl_3$; this yielded 3.20 g of **4b** (82%): mp > 300 °C; ^{1}H NMR ($CDCl_3$, 270 MHz): $\delta=8.58$ (s, 2H), 8.31 (s, 2H), 8.09 (s, 2H), 7.53 (t, $J=1.6$ Hz, 2H), 7.41 (d, $J=1.6$ Hz, 4H), 1.40 (s, 36H); ^{13}C NMR ($CDCl_3$, 67.5 MHz): $\delta=150.8$, 140.0, 138.6, 132.2, 128.8, 128.1, 127.2, 125.9, 125.4, 124.8, 121.5, 120.1, 35.1, 31.6; MS: *m/z* 737 (M^+). Anal. Calc. for $C_{44}H_{48}Br_2$: C, 71.74; H, 6.57; Br, 21.69. Found: C, 71.85; H, 6.46; Br, 21.78%.

3,8-Bis(3′,5′-di-*tert*-butylphenyl)-13,13,14,14-tetracyano-1,6-pyrenoquinodimethane 1a

A mixture of 200.0 mg of **4a**, 58.9 mg of tetracyanoethylene oxide (TCNEO) and 7 mL of freshly distilled 1,2-dibromoethane was refluxed for 3 h under nitrogen. After cooling to room temperature, the precipitated dark blue crystals were filtered off. This crude product was purified using silica gel chromatography eluting with CH_2Cl_2–hexane (1 : 1), yielding 38.0 mg of **1a**. The unreacted **4a** was recovered from the filtrate of the reaction mixture (160.0 mg). The estimated yield of **1a** was quantitative: mp >300 °C: ^{1}H NMR (270 MHz, $CDCl_3$): $\delta=9.39$ (d, $J=8.2$ Hz, 2H), 7.98 (d, $J=8.2$ Hz, 2H), 7.63 (t, $J=1.6$ Hz, 2H), 7.62 (s, 2H), 7.27 (d, $J=1.6$ Hz, 4H), 1.41 (s, 36H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 152.9, 151.7, 150.0, 135.5, 135.2, 131.4, 130.5, 130.1, 128.3, 127.7, 126.8, 123.9, 123.2, 116.4, 114.5, 35.2, 31.5; MS: *m/z* 706 (M + 1); IR (Nujol) ν_{CN} 2210 cm^{-1}. Anal. Calc. for $C_{50.3}H_{48.6}N_4Cl_{0.6}$ (**1a** $0.3CH_2Cl_2$): C, 82.71; H, 6.71; N, 7.67; Cl, 2.91. Found: C, 82.52; H, 6.84; N, 7.56; Cl, 2.95%. UV–VIS ($CHCl_3$): λ_{abs}/nm (log(ε/dm^3 mol^{-1} cm)) 607.0 (4.64), 558.0 (sh) (4.43), 430.0 (3.89), 317.0 (sh) (4.03), 293.5 (4.37), 265.0 (4.50).

3,6-Bis(3′,5′-di-*tert*-butylphenyl)-13,13,14,14-tetracyano-1,8-pyrenoquinodimethane 1b

A procedure similar to that described above was used for the synthesis of **1b** starting from 200.0 mg of **4b**, 58.0 mg of TCNEO and 7 mL of 1,2-dibromoethane; this yielded 22 mg of **1b** (quantitative) along with recovered **4b** (176.0 mg): mp >300 °C; ^{1}H NMR (270 MHz, $CDCl_3$): $\delta=9.58$ (s, 2H), 7.78 (s, 2H), 7.59 (br s, 2H), 7.26 (br s, 4H), 1.37 (s, 36H); ^{13}C NMR (67.5 MHz, $CDCl_3$): δ 152.3, 151.5, 150.6, 143.6, 135.8, 132.4, 131.6, 130.9, 128.9, 126.5, 123.7, 123.4, 118.5, 116.2, 35.1, 31.5; MS: *m/z* 706 (M + 1); IR (Nujol) ν_{CN} 2210 cm^{-1}. Anal. Calc. for $C_{50}H_{48}N_4$: C, 85.19; H, 6.86; N, 7.95. Found: C, 85.05; H, 6.59; N, 7.70%. UV–VIS ($CHCl_3$): λ_{abs} (log(ε/dm^3 mol^{-1} cm^{-1})) 647.0 (4.45), 472.0 (sh) (4.05), 409.0 (sh) (4.28), 382.5 (4.37), 365.0 (sh) (4.27), 302.0 (4.50), 292.0 (sh) (4.40).

Electron transfer salt 6

The complexation reaction was carried out in a glove box in the presence of < 1 ppm oxygen. A filtered hot solution of [Mn^{II}(TPP)]·py[23] (27.0 mg, 36.0 mmol) in 12.5 mL of boiling toluene was added to **1a** (26.0 mg, 37.0 mmol) dissolved in 12.5 mL of hot toluene. The solution was left to stand overnight, during which black–green crystals formed, which were collected by vacuum filtration and dried under vacuum for 3 h to give 15.0 mg (40%) of **6**.

X-Ray analysis

Data were collected on a Rigaku AFC5R four circle diffractometer system with graphite monochromated Mo-Kα radiation (50 kV, 200 mA, $\lambda=0.71069$ Å) equipped with a Rigaku low temperature device. The structures were solved by the teXsan crystallographic software package from Rigaku.[30]

Crystal data for 1b. $C_{54}H_{53}N_4$ (**1b** $0.5C_6H_4Me_2$-*p*), $M=758.04$, triclinic, space group $P\bar{1}$ (no. 2), $a=15.303(2)$, $b=15.294(2)$, $c=9.433(2)$ Å, $\alpha=100.16(2)$, $\beta=92.68(1)$, $\gamma=94.25(1)°$, $V=2163.1(7)$ Å^3, $Z=2$, $D_c=1.164$ g cm^{-3}, $T=-75.0(4)$ °C, $2\theta=55.0°$, R (R_w) = 0.061 (0.065), goodness-of-fit = 1.43, reflection/parameter ratio = 9.77 based on 5121 unique reflections with $I>2\sigma(I)$.

Crystal data for 3a. $C_{44}H_{50}$, $M=578.88$, triclinic, space group $P\bar{1}$ (no. 2), $a=9.833(1)$, $b=10.034(2)$, $c=9.428(1)$ Å, $\alpha=106.79(1)$, $\beta=97.32(1)$, $\gamma=95.49(1)°$, $V=874.5(3)$ Å^3, $Z=1$, $D_c=1.099$ g cm^{-3}, $T=-77.5(4)$ °C, $2\theta_{max}=55.0°$, R (R_w) = 0.052 (0.067), goodness-of-fit = 1.25, reflection/parameter ratio = 13.09 based on 2581 unique reflections with $I>\sigma(I)$.

Crystal data for 3b. $C_{44}H_{50}$, $M=578.88$, monoclinic, space group $C2/c$ (no. 15), $a=15.769(2)$, $b=11.552(2)$, $c=19.119(3)$ Å, $\beta=91.125(10)°$, $V=3482.1(9)$ Å^3, $Z=4$, $D_c=1.104$ g cm^{-3}, $T=-77.5(4)$ °C, $2\theta_{max}=55.0°$, R (R_w) = 0.064 (0.077), goodness-of-fit = 1.55, reflection/parameter ratio = 10.81 based on 2161 unique reflections with $I>\sigma(I)$.

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Full crystallographic details, excluding structure factors, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, 2000, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 1145/197.

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