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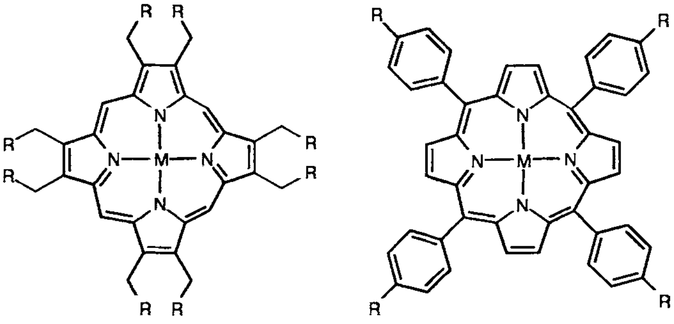
Low-Melting, Liquid-Crystalline Metalloporphyrins**

Qing Min Wang and Duncan W. Bruce*

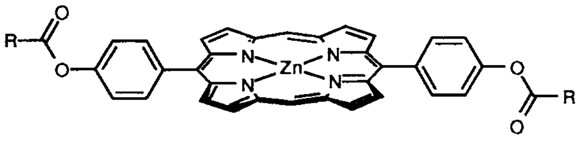
The inherent disklike shape of the porphyrin moiety led to initial work on liquid crystal porphyrins, which centered on peripherally octasubstituted systems (Scheme 1, left) that show columnar mesophases.[1] Later work on columnar systems by Shimizu and co-workers (Scheme 1, right) concentrated on *meso*-tetrasubstituted porphyrins, which showed lamello-columnar phases.[2] More recently, we became interested in trying to construct porphyrins that were extended in a more linear fashion, which we reasoned should lead to materials showing mesophases normally characteristic of rodlike (calamitic) molecules. Thus, we showed that zinc 5,15-di(alkoxyphenyl)porphyrins (**1a**) exhibited crystal smectic mesophases,[3] while the more extended zinc 5,15-di(4-(4-alkoxybenzoyloxy)phenyl)- (**1b**) and zinc 5,15-di(4-(4-alkylcyclohexanoyloxy)phenyl)porphyrins (**1c**) gave rise to nematic and smectic A mesophases, respectively.[4] Thus, by appropriate substitution of the porphyrin skeleton, control can be exerted over the molecular organization to lead either to columnar or calamitic mesophases.



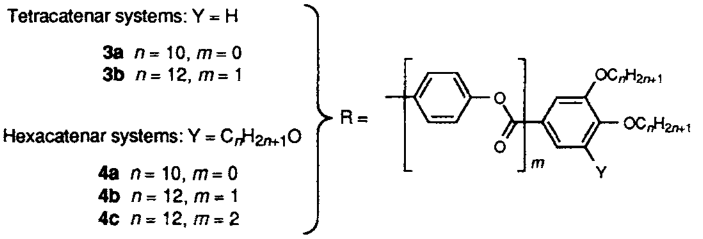
R = $CO_2C_nH_{2n+1}$
M = 2H, Zn
R = $CH_2OC_nH_{2n+1}$
M = 2H, Zn, Cd, Cu, Pd

R = C_nH_{2n+1}
M = 2H, Zn, Cu, VO, Co, Ni, Pd, Pt

Scheme 1. Porphyrins that form columnar mesophases.

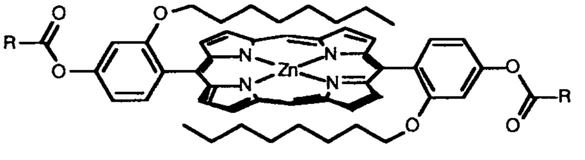


1a R = C_nH_{2n+1}
1b R = $C_nH_{2n+1}O-C_6H_4-CO$
1c R = $C_7H_{15}-C_6H_{10}-CO$

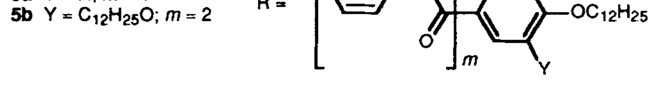


Tetracatenar systems: Y = H
3a $n = 10, m = 0$
3b $n = 12, m = 1$
Hexacatenar systems: Y = $C_nH_{2n+1}O$
4a $n = 10, m = 0$
4b $n = 12, m = 1$
4c $n = 12, m = 2$

However, the transition temperatures of the nematic and smectic A porphyrins were rather high (>300 °C), and we became interested in strategies to reduce these temperatures. Reduction of the transition temperatures is, of course, important both from the point of view of allowing in-depth physical studies, and for looking at potential applications (that is, having processable materials). In one approach[5] we had introduced lateral chains that folded over the faces of the porphyrin, acting as "lubrication", hence reducing intermolecular electrostatic interactions[6] and leading to lower melting and lower clearing materials (**2**). For example, **2a** (α,β-atropisomer, $n = 7$) melts at 141 °C to a nematic phase, which clears at 177 °C, whereas the parent porphyrin, **1b** ($n = 7$) melts into a nematic phase at 305 °C and clears with decomposition at 433 °C. In this paper, we describe another strategy, namely the synthesis of metalloporphyrins with several terminal alkyl chains (polycatenar[7]), which leads to materials with reduced melting points, and to another method of controlling the aggregation behavior of metalloporphyrins in mesophases. We also report that the combination of the "lubricating" and the polycatenar approach results in porphyrins with very low melting points.



2a R = $C_nH_{2n+1}O-C_6H_4-CO$
2b R = $C_7H_{15}-C_6H_{10}-CO$



5a Y = H; $m = 1$
5b Y = $C_{12}H_{25}O$; $m = 2$

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[**] This work was supported by a Sino-British Friendship Scholarship to Q. M. W.

The basic starting materials in this study were zinc 5,15-di(4-hydroxyphenyl)porphyrin and zinc 5,15-di(4-hydroxy-2-octyloxyphenyl)porphyrin, obtained from dipyrromethane[8] and 4-hydroxybenzaldehyde or 4-hydroxy-2-octyloxybenzaldehyde, respectively, as described previously.[4, 5] These were then treated with two equivalents of the appropriate benzoic acids in the presence of 4-(*N*,*N*-dimethylamino)pyridine and dicyclohexylcarbodiimide to give diesterified porphyrins.

The results obtained were at first sight a little disappointing in that only two of the seven new porphyrins were mesomorphic. The five-ring (four peripheral phenyl rings plus the porphyrin), tetracatenar material (**3a**) showed no mesophase at all, although its melting point was some 50 °C lower than that of a typical parent porphyrin with only one alkoxy chain at each end. Clearly here, the mesophase had been severely destabilized by the addition of the two terminal chains in the 3- and 3'- positions. The seven ring compound (**3b**) was mesomorphic and showed a smectic C and nematic phase. In principle, with dodecyloxy chains such a tetracatenar material would have been expected to show a columnar mesophase, in common with other tetracatenar materials. However, some studies have shown that columnar mesophases only arise when the molecular mass of the chain portion of the molecule is at least 50% of the total molecular mass.[9] In addition, there are few, if any, seven-ring tetracatenar mesogens for coomparison.

The hexacatenar materials are also rather devoid of mesomorphism, and both the five- (**4a**) and seven-ring (**4b**) systems were nonmesomorphic, although each showed several crystal modifications and much reduced melting points. However, the remarkable nine-ring material (**4c**) was in fact mesomorphic, forming a columnar mesophase between 188 and 288 °C. Given the very high molecular mass of this last porphyrin, this melting point is very low.

The most interesting porphyrins were obtained when the polycatenar strategy was combined with the approach in which lateral chains were used to lubricate the faces of the porphyrins.[5] The lateral chains act to prevent intermolecular $\pi-\pi$ interactions, so reducing both the melting and clearing point of the porphyrins.

The combination of the two approaches leads to the materials **5**, whose mesomorphic behavior is summarized in Table 1. Thus, **5a** melts into a nematic phase at 133 °C, clearing at 169 °C. The related parent with no lateral chains (**3b**) forms smectic C and nematic phases between 276 and 321 °C. Thus, the melting point has been reduced by 140 °C and the clearing point by 150 °C, while the smectic phase is suppressed. However, the massive nine-ring, hexacatenar porphyrin with lateral chains (**5b**) melts at only 50 °C into a nematic phase, clearing at 153 °C. Reductions in the melting and clearing points relative to the parent without a lateral chain (**4c**) were 138 and 135 °C, respectively, similar to the reductions observed for **5a**/**3b**. In this case, the columnar mesophase has been replaced by a fluid, nematic phase, and the melting point has been reduced to almost room-temperature—quite a drop from the first nematic porphyrins we reported with melting points in excess of 300 °C.[4]

It is interesting to note that in compounds **5**, there is no evidence for any complicating factors arising from atropisomerism. For related compounds, we were able to see clear evidence for transformations of one isomer into another by differential scanning calorimetry (DSC).[5b] The isomers were readily identified as the anisotropy of the α,β-isomer led to mesomorphic materials, while the greatly reduced anisotropy of the α,α-isomer precluded mesomorphism. Thus, although the ^{1}H NMR spectrum of **5a** showed some evidence of both α,α- and α,β-isomers in solution, the former obviously transformed easily into the latter on heating, as the material behaved as a pure compound. For **5b**, NMR showed only one isomer.

Table 1. Transition temperatures of the new porphyrins **3**–**5**.

Porphyrin	Transition [a]	T[°C]	ΔH[kJ mol^{-1}]	ΔS[J K^{-1} mol^{-1}]
3a	Cry-I	251	53.0	101
3b	Cry_1-Cry_2	138	2.4	6
	Cry_2-S_C	276	35.3	64
	S_C-N	287	2.0	4
	N-I [b]	321	–	
4a	Cry_1-Cry_2	58	3.1	9
	Cry_2-Cry_3	88	1.5	4
	Cry_3-Cry_4	120	5.0	13
	Cry_4-I	131	24.7	61
4b	Cry_1-Cry_2	54	1.8	6
	Cry_2-Cry_3	61	6.5	19
	Cry_3-I	164	60.4	138
4c	Cry_1-Cry_2	107	24.1	63
	Cry_2-ϕ	188	44.9	97
	ϕ-I	288	1.8	3
5a [c]	Cry-N	133	10.5	26
	N-I	169	1.6	4
5b	Cry-N	50	48.6	150
	N-I	153	0.7	2

[a] Abbreviations: Cry = crystalline phase, I = isotropic phase, S_C = smectic C phase, N = nematic phase, ϕ = columnar phase. The exact symmetry of the columnar mesophases has not yet been determined, although microscopy implies that it is hexagonal. [b] Decomposition occurred around T_{NI}. Thus, the TNI was obtained from microscopic observation. [c] The thermal data were obtained from the second heating. On the first heating, DSC thermogram was complicated by the phase transition from the α,α- to the α,β-atropisomer. However, on the second heating, the compound existed in the form of α,β-atropisomer.

The new strategy for the reduction of melting points in calamitic metalloporphyrins, namely the formation of polycatenar derivatives, leads on combination with the use of lateral chains to very low melting materials indeed. We are also able to control the nature of the mesophase formed in 5,15-disubstituted porphyrins by the use of the appropriate molecular design strategy, which is of particular significance for the design of materials with biaxial nematic mesophases. Materials with this phase have been postulated for molecules possessed of both rodlike and disklike features.[1] This work now provides us with materials whose potential biaxial properties can readily be evaluated, and we anticipate the results of these studies with great interest.

Experimental Section

The target porphyrins were prepared by a standard esterification between the appropriate carboxylic acid and zinc 5,15-di(4-hydroxyphenyl)porphyrin or zinc 5,15-di(4-hydroxy-2-octyloxyphenyl)porphyrin [5] with 4-(*N*,*N*-dimethylamino)pyridine (DMAP) and dicyclohexylcarbodiimide (DCC). The porphyrins were purified by flash chromatography and crystallization. Satisfactory spectroscopic and analytical data were obtained for all new compounds. Mesophases were characterized by optical microscopy (Zeiss Labpol equipped with a Linkam PR 600 controller and TH600 hot stage) and differential scanning calorimetry (Perkin Elmer DSC7).

4-(3,4-Di(dodecyloxy)benzoyloxy)benzoic acid: 3,4-Di(dodecyloxy)benzoic acid (1 g, 2.0 mmol), benzyl 4-hydroxybenzoate (0.5 g, 2.0 mmol), and DMAP (0.1 g, 1 mmol) were dissolved in a mixture of dichloromethane (30 mL) and THF (20 mL). To this solution, DCC (0.4 g, 2.0 mmol) and activated molecular sieves (4 or 5 Å, 2–3 g) were added. The mixture was stirred overnight at room temperature. The reaction solution was then filtered. On evaporation of solvents and crystallization from absolute ethanol, the pure product was obtained as a colorless, crystalline material (1.2 g, 80%). This compound (1.1 g, 1.6 mmol) was dissolved in freshly distilled THF. Palladium on charcoal (10%, 160 mg) was added. The solution was stirred at room temperature under 1 atm of H_2 for 3 h and then filtered through a pad of Celite to give a colorless solution. On evaporation of solvent and crystallization from absolute ethanol, the pure product was obtained as a colorless crystalline material (0.73 g, 73%). M.p. 147 °C. ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 0.87$ (t, 6H, $2CH_3$), 1.26 (m, 32H, $16CH_2$), 1.48 (m, 4H, $2CH_2$), 1.84 (m, 4H, $2CH_2$), 4.07 (m, 4H, $2OCH_2$), 6.93 (d, 1H, $J = 8.0$ Hz), 7.33 and 8.20 (m, 4H, benzene ring, AA'XX', $J_{AX} = 9$ Hz), 7.65 (d, 1H, $J = 2$ Hz), 7.82 (dd, 1H, $J = 8$, $J' = 2$ Hz). Elemental analysis (%): found: C 74.8, H 9.6; required for $C_{38}H_{58}O_6$: C 74.7, H 9.6.

4-(3,4,5-Tri(dodecyloxy)benzoyloxy)benzoic acid: The synthesis was as above, starting with 3,4,5-tridodecyloxybenzoic acid. Yields: esterification: 92%; hydrogenolysis: 75%. M.p. 92 °C. ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 0.87$ (m, 9H, $3CH_3$), 1.26 (m, 48H, $24CH_2$), 1.49 (m, 6H, $3CH_2$), 1.83 (m, 6H, $3CH_2$), 4.04 (m, 6H, $3OCH_2$), 7.40 (s, 2H, benzene ring), 7.32 and 8.20 (m, 4H, benzene ring, AA'XX', $J_{AX} = 9$ Hz). Elemental analysis (%): found C 75.7, H 10.9; required for $C_{50}H_{82}O_7$: C 75.5, H 10.4.

4-(3,4,5-Tri(dodecyloxy)benzoyloxy)benzoyloxybenzoic acid: The synthesis was as above, starting with 3,4,5-tridodecyloxybenzoic acid; esterification/hydrogenolysis was repeated to obtain this compound. Yields: esterification: 97%; hydrogenolysis: 86%. M.p. 90 °C. ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 0.87$ (m, 9H, $3CH_3$), 1.26 (m, 48H, $24CH_2$), 1.49 (m, 6H, $3CH_2$), 1.84 (m, 6H, $3CH_2$), 4.05 (m, 6H, $3OCH_2$), 7.41 (s, 2H, benzene ring), 7.35, 7.38, 8.21, 8.29 (m, 8H, two benzene rings, two AA'XX' systems, $J_{AX} = 9$ Hz). Elemental analysis (%): found C 74.8, H 9.6; required for $C_{57}H_{86}O_9$: C 74.8, H 9.5.

Porphyrin **3a**: $\delta = 0.90$ (t, 12H, $4CH_3$), 1.25–1.54 (m, 56H, $28CH_2$), 1.94 (m, 8H, $4CH_2$), 4.17 (m, 8H, $4OCH_2$), 7.05 (d, 2H, $J = 8.5$ Hz), 7.65 and 8.34 (m, 8H, two inner benzene rings, AA'XX', $J = 8.5$ Hz), 7.88 (d, 2H, $J = 2$ Hz), 8.04 (dd, 2H, $J = 8.5$, $J' = 2$ Hz), 9.24 and 9.49 (d, 8H, 8βH, AB, $J = 5$ Hz), 10.39 (s, 2H, 2*meso*-H). Yield 30%. UV/Vis (CH_2Cl_2): $\lambda_{max} = 411.1$, 539.3, 574.4 nm. C,H,N analysis: found(calcd): C 74.2(74.3), H 7.8(7.8), N 3.9(4.0). FAB-MS (positive ions): *m/z*: 1391 [M^+] (calcd: 1391.22).

Porphyrin **3b**: $\delta = 0.89$ (t, 12H, $4CH_3$), 1.20–1.50 (m, 72H, $36CH_2$), 1.88 (m, 8H, $4CH_2$), 4.10 (m, 8H, $4OCH_2$), 6.97 (d, 2H, $J = 8.5$ Hz), 7.49 and 8.34 (m, 8H, two inner benzene rings, AA'XX', $J = 8.5$ Hz), 7.69 and 8.50 (m, 8H, two middle benzene rings, AA'XX', $J = 8.5$ Hz), 7.71 (d, 2H, $J = 2$ Hz), 7.88 (dd, 2H, $J = 8.5$, $J' = 2$ Hz), 9.21 and 9.47 (d, 8H, 8βH, AB, $J = 4.6$ Hz), 10.35 (s, 2H, 2*meso*-H). Yield 61%. UV/Vis (CH_2Cl_2): $\lambda_{max} = 410.5$, 538.9, 574.4 nm. C,H,N analysis: found(calcd): C 74.2(74.4), H 7.7(7.6), N 2.9(3.2). FAB-MS (positive ions): *m/z*: 1743 [M^+] (calcd: 1743.66).

Porphyrin **4a**: $\delta = 0.90$ (t, 18H, $6CH_3$), 1.20–1.52 (m, 84H, $42CH_2$), 1.88 (m, 12H, $6CH_2$), 4.15 (m, 12H, $6OCH_2$), 7.62 (s, 4H), 7.65 and 8.33 (m, 8H, two inner benzene rings, AA'XX', $J = 8.5$ Hz), 9.21 and 9.49 (d, 8H, 8βH, AB, $J = 4.6$ Hz), 10.37 (s, 2H, 2*meso*-H). Yield 51%. UV/Vis (CH_2Cl_2): $\lambda_{max} = 410.6$, 539.2, 574.4 nm. C,H,N analysis: found(calcd): C 74.5(74.7), H 9.0(8.8), N 3.2(3.3). FAB-MS (positive ions): *m/z*: 1703 [M^+] (calcd: 1703.6).

Porphyrin **4b**: $\delta = 0.82$ (t, 18H, $6CH_3$), 1.16–1.46 (m, 108H, $54CH_2$), 1.76 (m, 12H, $6CH_2$), 4.03 (t, 12H, $6OCH_2$), 7.40 (s, 4H), 7.42 and 8.28 (m, 8H, two inner benzene rings, AA'XX', $J = 8.2$ Hz), 7.63 and 8.44 (m, 8H, two middle benzene rings, AA'XX', $J = 8.5$ Hz), 9.16 and 9.43 (d, 8H, 8βH, AB, $J = 4.6$ Hz), 10.31 (s, 2H, 2*meso*-H). Yield 56%. UV/Vis (CH_2Cl_2): $\lambda_{max} = 410.7$, 539.2, 574.4 nm. C,H,N analysis: found(calcd): C 75.0(75.1), H 8.5(8.5), N 2.6(2.7). FAB-MS (positive ions): *m/z*: 2111 [$(M-1)^+$] (calcd: 2112.3).

Porphyrin **4c**: $\delta = 0.88$ (t, 18H, $6CH_3$), 1.22–1.52 (m, 108H, $54CH_2$), 1.82 (m, 12H, $6CH_2$), 4.07 (t, 12H, $6OCH_2$), 7.43 (s, 4H), 7.41, 7.52, 7.69, 8.35, 8.36, 8.52 (m, 24H, six benzene rings, three AA'XX' systems, $J = 8.2$–8.9 Hz), 9.22 and 9.49 (d, 8H, 8βH, AB, $J = 4.6$ Hz), 10.37 (s, 2H, 2*meso*-H). Yield 55%. UV/Vis (CH_2Cl_2): $\lambda_{max} = 410.4$, 538.5, 574.8 nm. C,H,N analysis: found(calcd): C 74.0(74.5), H 8.0(8.1), N 2.3(2.4). FAB-MS (positive ions): *m/z*: 2351 [$(M-1)^+$] (calcd: 2352.52).

Porphyrin **5a**: $\delta = 0.32$ (m, protons of the terminal methyl groups of the lateral side chains), 0.36–1.06 (m, 36H, $4CH_3 + 12CH_2$ in the lateral chains), 1.22–1.52 (m, 72H, $36CH_2$), 1.89 (m, 8H, $4CH_2$), 3.91 (t with tiny couplings, 4H, $2OCH_2$ in the lateral chains), 4.11 (m, 8H, $4OCH_2$), 6.98 (d, 2H, $J = 8.6$ Hz), 7.26 (m, overlapped with the $CHCl_3$ signal, 2H), 7.31 (d, 2H, $J = 2.2$ Hz), 7.49 and 8.49 (m, 8H, two middle benzene rings, AA'XX', $J = 8.5$ Hz), 7.72 (d, 2H, $J = 2.1$ Hz), 7.89 (dd, 2H, $J = 8.6$, $J' = 2.1$ Hz), 8.12 and 8.15 (d in two sets, 2H, $J = 7.6$ Hz), 9.15 (d in two sets, 4H, 4βH, AB, $J = 4.6$ Hz), 9.42 (d, 4H, 4βH, AB, $J = 4.6$ Hz), 10.29 (s, 2H, 2*meso*-H). Yield 61%. UV/Vis (CH_2Cl_2): $\lambda_{max} = 410.4$, 538.5, 573.7 nm. C,H,N analysis: found(calcd): C 74.0(74.5), H 8.4(8.3), N 2.7(2.8). FAB-MS (positive ions): *m/z*: 1999 [$(M-1)^+$] (calcd: 2000.09).

Porphyrin **5b**: $\delta = 0.33$ (m, protons of the terminal methyl groups of the lateral side chains), 0.36–1.08 (m, 42H, $6CH_3 + 12CH_2$ in the lateral chains), 1.27 (m, 96H, $48CH_2$), 1.51 (m, 12H, $6CH_2$), 1.82 (m, 12H, $6CH_2$), 3.91 (t, 4H, $2OCH_2$ in the lateral chains), 4.07 (m, 12H, $6OCH_2$), 7.26 (m, overlapped with the $CHCl_3$ signal, 2H), 7.31 (d, 2H, $J = 1.9$ Hz), 7.43 (s, 4H), 7.41, 7.51, 8.36, 8.51 (m, 16H, four middle benzene rings, two AA'XX' systems, $J = 8.9$ Hz), 8.12 and 8.15 (d in two sets, 2H, $J = 7.3$ Hz), 9.14 (d in two sets, 4H, 4βH, AB, $J = 4.6$ Hz), 9.42 (d, 4H, 4βH, AB, $J = 4.6$ Hz), 10.28 (s, 2H, 2*meso*-H). Yield 55%. UV/Vis (CH_2Cl_2): $\lambda_{max} = 410.9$, 539.2, 574.4 nm. C,H,N analysis: found(calcd): C 74.1(74.6), H 8.5(8.5), N 2.4(2.2). FAB-MS (positive ions): *m/z*: 2609 [M^+] (calcd: 2608.95).

Received: April 30, 1996
Revised version: October 2, 1996 [Z9083IE]
German version: *Angew. Chem.* **1997**, *109*, 102–105

Keywords: liquid crystals · nematic phases · porphyrinoids

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Valence-Delocalized and Valence-Trapped $Fe^{II}Fe^{III}$ Complexes: Drastic Influence of the Ligands

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Complexes with metal ions in mixed oxidation states play important roles in materials and biology.[1] The valence-trapped $Fe^{II}Fe^{III}$ units are known to occur in the diiron proteins hemerythrin, methane monoxygenase, and purple acid phosphatase, in which the two high-spin metal centers are antiferromagnetically coupled with an $S = 1/2$ ground state.[2] By contrast, the presence of a valence-delocalized $[Fe_2]^V$ unit with $S = 9/2$ spin ground state has been implicated[3] in iron–sulfur proteins containing $[Fe_2S_2]$, $[Fe_3S_4]$ and $[Fe_4S_4]^{3-}$ cores. The domineering influence of double exchange,[4] that is, the interplay of electron transfer and electron coupling, on electronic and magnetic properties of valence-delocalized species has been underscored by several theoretical studies.[5]

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