Supporting Information

belonging to

Organization of spin- and redox-labile metal centers into Langmuir and Langmuir-Blodgett films

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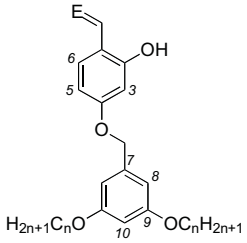
1. Synthetic details

Synthesis of 3e. A suspension of 2,4-hydroxybenzaldehyde (1.40 g, 10.1 mmol), KI (328 mg, 2.0 mmol) and $NaHCO_3$ (1.08 g, 12.8 mmol) in MeCN (140 mL) was stirred at 70°C during 15 min. A warm solution of corresponding benzyl bromide **2e** (4.0 g, 9.4 mmol) in dry THF (60 mL) was slowly added and stirring at reflux was continued for 3 d. The formed precipitate was filtered and washed with THF. The combined filtrates were evaporated *in vacuo* and the residue was purified by gradient column chromatography (SiO_2, hexane to hexane/EtOAc 9:1). The title compound was obtained as a yellow oil (3.87 g, 85%). Upon standing some white crystals formed, which were collected, washed with EtOH and dried *in vacuo*. M.p. 42 °C. ^{1}H NMR ($CDCl_3$, 360 MHz): δ 11.46 (s, 1H, OH), 9.72 (s, 1H, CHO), 7.44 (d, 1H, J = 8.7 Hz, C^6H), 6.61 (d, 1H, J = 8.7 Hz, C^5H), 6.52 (s, 2H, C^8H), 6.49 (s, 1H, C^3H), 6.41 (m, 2H, C^{10}H), 5.03 (s, 2H, $C^{ar}CH_2O$), 3.93 (t, 4H, J = 6.3 Hz, $CH_2C\mathit{H}_2O$), 1.76 (m, 4H, $C\mathit{H}_2CH_2O$), 1.5–1.4 (m, 4H, $C\mathit{H}_2CH_2CH_2O$), 1.4–1.2 (m, 16H, all CH_2), 0.88 (t, 6H, J = 6.7 Hz, CH_3). ^{13}C NMR ($CDCl_3$, 90 MHz): δ 194.6 (CHO), 166.0, 164.6 (2 × $C^{ar}O$), 160.8 (C^9), 137.9 (C^7), 135.4 (C^6H), 115.5 (*C*CHO), 109.1 (C^5H), 105.8 (C^8H), 101.8 (C^3H), 101.1(C^{10}H), 70.5 (OCH_2C^{ar}), 68.2 (OCH_2), 32.5–29.0, 22.8 (all CH_2), 29.5 (OCH_2CH_2), 26.2 ($OCH_2CH_2CH_2$), 14.3 (CH_3). HR–MS (ESI, Acetone): Calcd. for $C_{30}H_{43}O_5$ $[M - H]^-$ m/z = 483.3116, found m/z = 483.3105. Anal. found (calcd) for $C_{30}H_{44}O_5$ (484.68): C 74.41 (74.34); H 9.17 (9.15)



Synthesis of 3f. According to the method described for **3e**, a suspension of 2,4-hydroxybenzaldehyde (1.26 g, 8.9 mmol), KI (296 mg, 1.8 mmol) and $NaHCO_3$ (974 mg, 11.6 mmol) in MeCN (125 mL) was reacted with **2f** (3.61 g, 6.7 mmol) in THF (60 mL). The title compound was obtained as a white solid (2.15 g, 54%). M.p. 60°C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 11.46 (s, 1H, OH), 9.71 (s, 1H, CHO), 7.43 (d, 1H, J = 8.7 Hz, C^6H), 6.60 (dd, 1H, J = 8.7, 2.3 Hz, C^5H), 6.52 (d, 2H, J = 1.8 Hz, C^8H), 6.49 (d, 1H, J = 2.4 Hz, C^3H), 6.41 (t, 2H, J = 2.3 Hz, C^{10}H), 5.02 (s, 2H, $C_{ar}CH_2O$), 3.93 (t, 4H, J = 6.6 Hz, $CH_2C\mathit{H}_2O$), 1.81–1.71 (m, 4H, $C\mathit{H}_2CH_2O$), 1.49–1.39 (m, 4H, $C\mathit{H}_2CH_2CH_2O$), 1.39–1.19 (m, 32H, all CH_2), 0.88 (t, 6H, J = 7.0 Hz, CH_3). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 194.6 (CHO), 166.0, 164.6 (2 × $C^{ar}O$), 160.8 (C^9), 137.9 (C^7), 135.4 (C^6H), 115.8 (*C*CHO), 109.1 (C^5H), 105.8 (C^8H), 101.8 (C^3H), 101.1(C^{10}H), 70.5 (OCH_2C^{ar}), 68.2 (OCH_2), 32.1–29.0, 22.8 (all CH_2), 29.5 (OCH_2CH_2), 26.2 ($OCH_2CH_2CH_2$), 14.3 (CH_3). MS (ESI): m/z = 619.4 $[M + Na]^+$. Anal. found (calcd) for $C_{38}H_{60}O_5$ (596.88): C 76.36 (76.47); H 10.22 (10.13).

Synthesis of 3g. According to the method described for **3e**, a suspension of 2,4-hydroxybenzaldehyde (2.27 g, 16.1 mmol), KI (534 mg, 3.2 mmol) and $NaHCO_3$ (1.76 g, 20.9 mmol) in MeCN (460 mL) was reacted with **2g** (8.54 g, 12.1 mmol) in THF (200 mL). After filtration of the reaction mixture, the combined filtrates were concentrated to ca. 150 mL and stored at 4°C for 1h. A precipitate formed, which was collected, washed with EtOH, and dried *in vacuo* to give **3g** (6.78 g, 73%). M.p. 73 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 11.45 (s, 1H, OH), 9.71 (s, 1H, CHO), 7.43 (d, 1H, J = 8.7 Hz, C^6H), 6.60 (dd, 1H, J = 8.7, 2.3 Hz, C^5H), 6.52 (d, 2H, J = 1.8 Hz, C^8H), 6.49 (d, 1H, J = 2.3 Hz,

C^3H), 6.41 (t, 2H, J = 2.3 Hz, $C^{10}H$), 5.02 (s, 2H, $C^{ar}CH_2O$), 3.93 (t, 4H, J = 6.6 Hz, CH_2CH_2O), 1.81–1.71 (m, 4H, CH_2CH_2O), 1.49–1.39 (m, 4H, $CH_2CH_2CH_2O$), 1.39–1.19 (m, 56H, all CH_2), 0.88 (t, 6H, J = 7.0 Hz, CH_3). ^{13}C NMR ($CDCl_3$, 90 MHz): δ 194.6 (CHO), 166.0, 164.6 (2 × $C^{ar}O$), 160.8 (C^9), 137.9 (C^7), 135.4 (C^6H), 115.8 (*C*CHO), 109.1 (C^5H), 105.8 (C^8H), 101.8 (C^3), 101.1(C^{10}), 70.5 (OCH_2C^{ar}), 68.2 (OCH_2), 32.1–29.0, 22.8 (all CH_2), 29.5 (OCH_2CH_2), 26.2 ($OCH_2CH_2CH_2$), 14.3 (CH_3). MS (ESI): m/z = 763.7 $[M – H]^-$. Anal. found (calcd) for $C_{50}H_{84}O_5$: C 78.51 (78.48); H 11.07 (11.06)

Synthesis of 4c. To a solution of **3c** (2.24 g, 7.3 mmol) in warm EtOH (150 mL) were added $MgSO_4$ (2.90 g, 24.1 mmol) and triethylenetetramine (0.55 mL, 3.65 mmol). The mixture was stirred at reflux for 16 h under an Ar atmosphere. Subsequently the precipitate was rapidly filtered, rinsed with EtOH (3 × 10 mL) and the combined filtrates were concentrated to 40 mL. Upon cooling to –25°C a precipitate slowly formed, which was collected by filtration, washed with cold EtOH (3 × 30 mL) and dry Et_2O (2 × 30 mL). After drying *in vacuo*, **4c** was obtained as an off-white solid (1.30 g, 49%). M.p. 118–121 °C. IR ($CHCl_3$): 1632 (C=N), 1605 cm^{-1} (C=C). ^1H NMR ($CDCl_3$, 360 MHz): δ 8.08 (s, 2H, N=CH), 6.93 (d, 2H, J = 8.6 Hz, C^6H), 6.19 (d, 2H, J = 2.2 Hz, C^3H), 6.04 (dd, 2H, J = 8.6, 2.3 Hz, C^5H), 4.09–3.95 (m, 2H, CH_2N=), 3.88 (t, 4H, J = 6.7 Hz, OCH_2), 3.41–3.24 (m, 4H, CH_2N= and CH_2CH_2N=), 2.91–2.78 (m, 2H, NCH_2CH_2N), 2.57–2.37 (m, 4H, CH_2CH_2N= and NCH_2CH_2N), 1.92 (s, 2H, NH), 1.83-1.55 (m, 4H, OCH_2CH_2), 1.46–1.35 (m, 4H, $OCH_2CH_2CH_2$), 1.35–1.12 (m, 56H, CH_2), 0.87 (t, 6H, J = 6.7 Hz, CH_3), OH not resolved. ^{13}C NMR ($CDCl_3$, 50 MHz): δ 172.5, 164.0 (2 × $C^{ar}O$), 167.1 (N=CH), 135.5 (C^6H), 115.3 (*C*CHN), 105.2 (C^5H), 102.6 (C^4H), 67.6 (OCH_2), 55.8 (CH_2N=), 47.4 (CH_2CH_2N=), 44.4 (NCH_2CH_2N), 32.0, 30.0–29.3, 22.8 (all CH_2), 29.4 (OCH_2CH_2), 26.2 ($OCH_2CH_2CH_2$), 14.3 (CH_3). HR–MS (ESI): calcd for $C_{44}H_{75}N_4O_4$ $[M + H]^+$ m/z = 723.5783, found m/z = 723.5783.

Synthesis of 4d. A solution of **3d** (3.27 g, 8.37 mmol) in warm EtOH/THF 2:1 (60 mL) was added to a suspension of triethylenetetramine (612 mg, 4.18 mmol) and $MgSO_4$ (3.00 g) in EtOH (60 mL). The mixture was heated to reflux for 16 h under Ar and subsequently filtered. The residue was rinsed with EtOH (2 × 30 mL) and the product was extracted from the filter with THF (3 × 75 mL) to give, after evaporation of the solvent, the pale yellow solid **4d** (2.51 g, 67%). M.p. 122–124 °C. IR ($CHCl_3$): 1634 (C=N), 1605 cm^{-1} (C=C). ^1H NMR ($CDCl_3$, 360 MHz): δ 8.07 (s, 2H, N=CH), 6.92 (d, 2H, J = 8.6 Hz, C^6H), 6.19 (d, 2H, J = 2.2 Hz, C^3H), 6.03 (dd, 2H, J = 8.6, 2.3 Hz, C^5H), 4.09–3.95 (m, 2H, CH_2N=), 3.88 (t, 4H, J = 6.6 Hz, OCH_2), 3.41–3.24 (m, 4H, CH_2N= and CH_2CH_2N=), 2.93–2.76 (m, 2H, NCH_2CH_2N), 2.59–2.35 (m, 4H, CH_2CH_2N= and NCH_2CH_2N), 1.90 (s, 2H, NH), 1.80-1.65 (m, 4H, OCH_2CH_2), 1.50–1.35 (m, 4H, $OCH_2CH_2CH_2$), 1.35–1.12 (m, 56H, CH_2), 0.88 (t, 6H, J = 6.7 Hz, CH_3), OH not resolved. ^{13}C NMR ($CDCl_3$, 90 MHz): δ 172.5, 164.1 (2 × $C^{ar}O$), 167.1 (N=CH), 135.6 (C^6H), 115.3 (*C*CHN), 105.2 (C^5H), 102.6 (C^3H), 67.6 (OCH_2), 55.8 (CH_2N=), 47.4 (CH_2CH_2N=), 44.5 (NCH_2CH_2N), 32.1, 30.2–29.8, 22.8 (all CH_2), 29.7 (OCH_2CH_2), 26.2 ($OCH_2CH_2CH_2$), 14.3 (CH_3). Anal. found (calcd) for $C_{56}H_{98}N_4O_4$ (891.76) × $MgSO_4$: C 66.30 (66.48); H 9.66 (9.76); N 5.64 (5.54). HR–MS (ESI): calcd for $C_{56}H_{99}N_4O_4$ $[M + H]^+$ m/z = 891.7661, found m/z = 891.7664.

2. Representative CV of Co(III) complexes

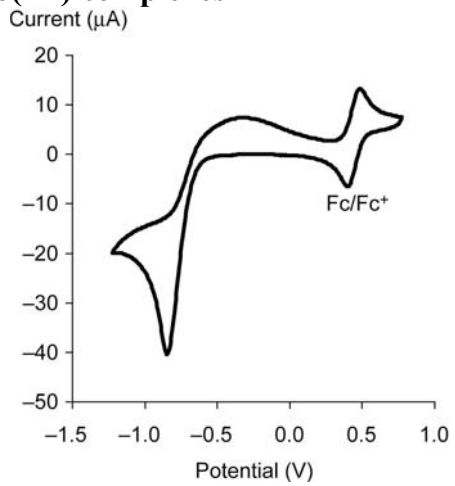


Figure S1. Representative cyclic voltammogram of complex **6d** indicating the irreversible reduction of the cobalt center.

3. Langmuir film characteristics

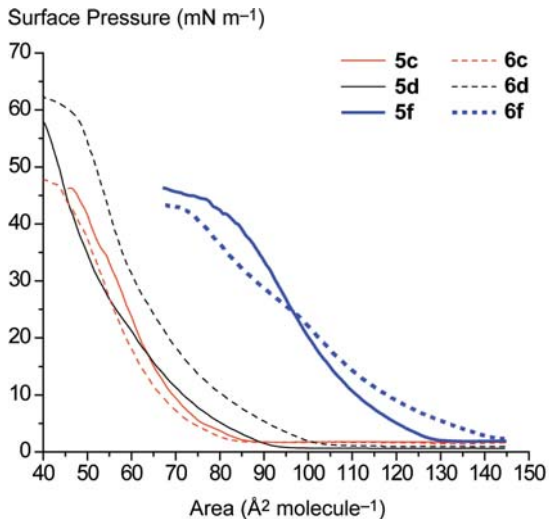


Figure S2. Representative pressure-area isotherms for the cobalt complexes **5c**, **5d**, and **5f** containing a Cl^- anion, and for the analogous complexes **6c**, **6d**, and **6f** containing a NO_3^- anion.

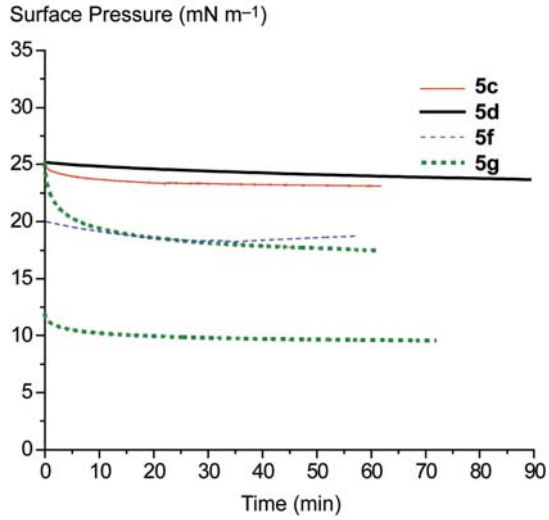


Figure S3. Film stability deduced from the time-dependent pressure change at a fixed area.

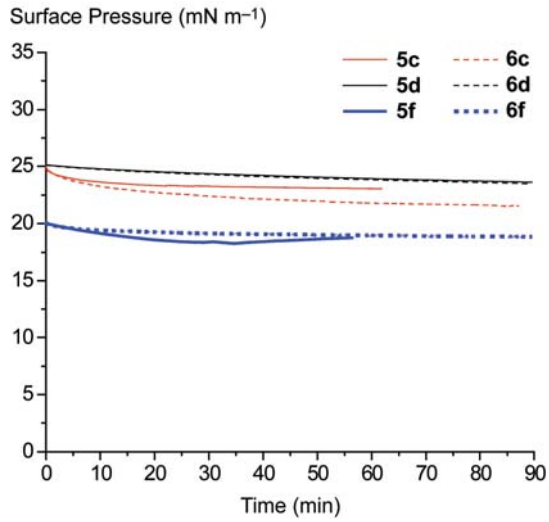


Figure S4. Stability of films comprising cobalt complexes comprising Cl^- (**5**) and NO_3^- (**6**) anions, respectively, as deduced from the time-dependent pressure change at a fixed area.

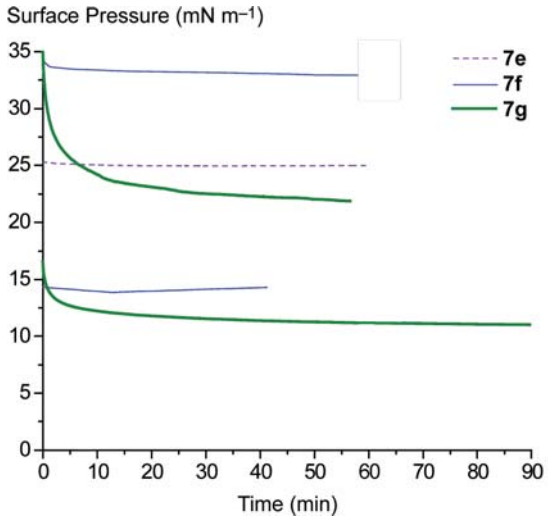


Figure S5. Time-dependent change of the surface pressure at a fixed area, indicating the different stability of films composed of iron complexes **7e–g** at different initial compression.

4. UV-vis measurement of bilayer LB film

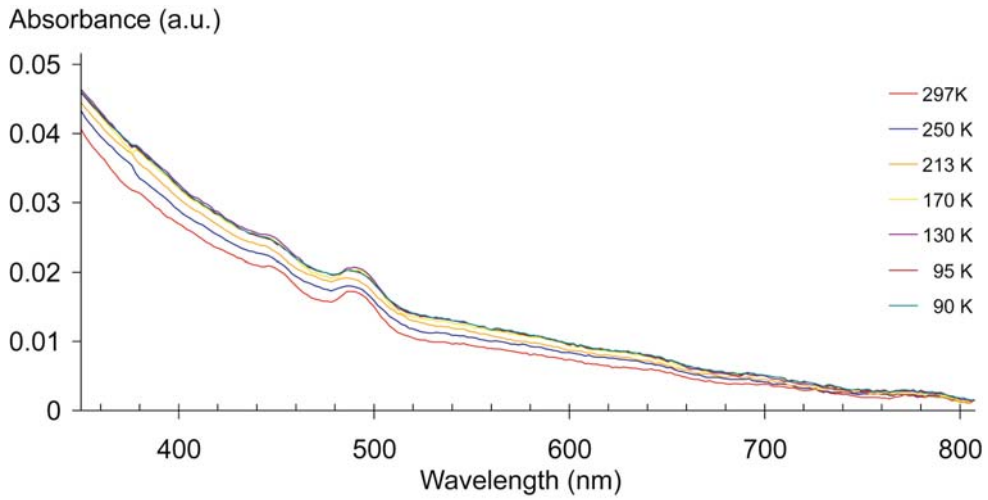


Figure S6. Superimposed absorption spectra of bilayers of complex **7d** in the visible range, illustrating a change in adsorption in the 250-170 K range. Addition of further layers is prevented by the partial desorption of the second layer, thus leading to a maximum coating of two complete layers on the support (cf. transfer ratios, Table 2 and Fig. 6 in the article).