

Supporting Information for

Zippering Up Fullerenes into Polymers Using Rhodium(II) Acetate Dimer and $N(\text{CH}_2\text{CH}_2)_2\text{NC}_{60}$ as Building Blocks

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Experimental section:

Synthesis of $N(\text{CH}_2\text{CH}_2)_2\text{NC}_{60}$. Fullerene C_{60} was functionalized with piperazine ($\text{N}_2\text{C}_4\text{H}_4$) as described previously.¹ Dianthracene was prepared in a photochemical reaction of anthracene in benzene under nitrogen atmosphere.²

$\{\text{Rh}_2(\text{O}_2\text{CCH}_3)_4\text{N}(\text{CH}_2\text{CH}_2)_2\text{NC}_{60}\}_n \cdot 2n\text{CS}_2$ (1). A saturated solution of 2.1 mg (0.0026mmol) of $N(\text{CH}_2\text{CH}_2)_2\text{NC}_{60}$ in 1.2 mL carbon disulfide was added to a 6 mm glass tube and layered with 0.4 mL of a saturated solution of triptycene or anthracene dimer in acetone. A saturated solution of 1.16 mg (0.0026 mmol) rhodium acetate dimer, $\text{Rh}_2(\text{O}_2\text{CCH}_3)_4$, in 1 mL of acetone was also filtrated and slowly added to the tube. After standing for two weeks black, single crystals of the polymer, $\{\text{Rh}_2(\text{O}_2\text{CCH}_3)_4\text{N}(\text{CH}_2\text{CH}_2)_2\text{NC}_{60}\}_n \cdot 2n\text{CS}_2$, formed at the interface of the solutions. The yield was 48% based on recovered starting material.

Infrared spectrum: 495 s, 522s, 564 w, 588 w, 615 w, 688s, 738w, 816m, 851m, 911w, 961w, 1029w, 1091 w, 1336w, 1406s, 1504s, 1585s, 1648w, 2833w, 2887w, 2943w, 2975w cm^{-1}

$\{\text{Rh}_2(\text{O}_2\text{CCH}_3)_4\text{N}(\text{CH}_2\text{CH}_2)_2\text{NC}_{60}\}_n \cdot n\text{C}_{60} \cdot 2n\text{CS}_2$ (2). A saturated solution of 2.1 mg (0.0026mmol) of $N(\text{CH}_2\text{CH}_2)_2\text{NC}_{60}$ in 1.2 mL carbon disulfide was layered with a saturated solution of 1.87 mg (0.0026mmol) of C_{60} in 1 mL carbon disulfide in a 6 mm glass tube. Triptycene/anthracene dimer and rhodium acetate dimer solutions were filtrated and added in order into the tube as mentioned before. After standing for two weeks black, single crystals of the polymer, $\{\text{Rh}_2(\text{O}_2\text{CCH}_3)_4\text{N}(\text{CH}_2\text{CH}_2)_2\text{NC}_{60}\}_n \cdot n\text{C}_{60} \cdot 2n\text{CS}_2$, formed at the interface of the solutions. The yield was 43% based on recovered starting material.

Infrared spectrum: 496 s, 522s, 564 m, 588w, 615 w, 690s, 737w, 816m, 852s, 914w, 963m, 1032w, 1093w w, 1339m, 1406s, 1504s, 1585s, 1648w, 1683w, 2850w, 2915w cm^{-1}

$\{\text{Rh}_2(\text{O}_2\text{CCH}_3)_4\text{N}(\text{CH}_2\text{CH}_2)_2\text{NC}_{60}\}_n \cdot n\text{C}_{70}$ (3), A saturated solution of 2.1 mg (0.0026mmol) of $N(\text{CH}_2\text{CH}_2)_2\text{NC}_{60}$ in 1.2 mL carbon disulfide was layered with a saturated solution of 2.1 mg (0.0026mmol) of C_{70} in 1 mL carbon disulfide in a 6 mm glass tube. Triptycene/anthracene dimer and rhodium acetate dimer solutions were layered in order as mentioned before. After standing for a month black, single crystals of the polymer, $\{\text{Rh}_2(\text{O}_2\text{CCH}_3)_4\text{N}(\text{CH}_2\text{CH}_2)_2\text{NC}_{60}\}_n \cdot n\text{C}_{70}$, formed at the interface of the solutions. The yield was 57% based on recovered starting material.

Infrared spectrum: 438 m, 492 s, 521s, 568 m, 609 w, 615 w, 690m, 740w, 791w, 810w, 851m, 914w, 949w, 1003w, 1029w, 1081w, 1119w, 1172w, 1217w, 1248w, 1290w, 1345m, 1406s, 1423s, 1454w, 1507m, 1582s, 1642w, 1709m, 2850w, 2923w, 2960w cm⁻¹

1) (a) Kampe, K. D.; Egger, N.; Vogel, M. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1174-1176. (b) Kampe, K. D.; Egger, N. *Liebigs Ann. Chem.* **1995**, 115-124. (c) Balch, A. L.; Cullison, B.; Fawcett, W. R.; Ginwalla, A. S.; Olmstead, M. M.; Winkler, K. *J. Chem. Soc., Chem. Commun.* **1995**, 2287-2288.

2) Breton, G.W.; Vang, X. *J. Chem. Ed.* **1998**, *75*, 81-82.

Crystallographic information:

Crystal data for {Rh₂(O₂CCH₃)₄N(CH₂CH₂)₂NC₆₀}_n•2nCS₂ (1) at 90 K (CCDC 1016156). C₃₇H₁₀NO₄RhS₂: *M* = 699.49, black block, 0.049 × 0.031 × 0.200 mm, λ=0.71073 Å, orthorhombic, space group *Pnma* (no. 62), *a* = 15.7899(14), *b* = 19.3598(17), *c* = 15.8920(14) Å, *T* = 90(2) K, *V* = 4858.0(7) Å³, *Z* = 4, 45943 reflections measured, 4762 unique (*R*_{int} = 0.0175) which were used in all calculations, Bruker Apex II; 2θ_{max} = 66.88°; min/max transmission = 0.649/0.747 (multi-scan absorption correction applied); direct and Patterson methods solution; full-matrix least squares based on *F*² (SHELXT and SHELXL-2012); The final *wR*(*F*₂) was 0.0847 (all data), conventional *R*₁ = 0.0322 computed for 4681 reflections with *I* > 2σ (*I*) using 413 parameters with no restraints.

Crystal data for {Rh₂(O₂CCH₃)₄N(CH₂CH₂)₂NC₆₀}_n•nC₆₀•2nCS₂ (2) at 90 K (CCDC 1016153). C₁₃₄H₂₀N₂O₈Rh₂S₄: *M* = 2119.58, black block, 0.136 × 0.117 × 0.039 mm, λ = 1.54178 Å, orthorhombic, space group *Pnma* (no. 62), *a* = 19.2432(8), *b* = 19.6828(8), *c* = 19.9173(9) Å, *T* = 90(2) K, *V* = 7543.9(6) Å³, *Z* = 4, 64991 reflections measured, 7122 unique (*R*_{int} = 0.0427) which were used in all calculations, Bruker Apex DUO; 2θ_{max} = 136.83°; min/max transmission = 0.534/0.821 (multi-scan absorption correction applied); direct and Patterson methods solution; full-matrix least squares based on *F*² (SHELXT and SHELXL-2012); The final *wR*(*F*₂) was 0.1748 (all data), conventional *R*₁ = 0.0603 computed for 6611 reflections with *I* > 2σ (*I*) using 685 parameters with 76 restraints.

Crystal data for {Rh₂(O₂CCH₃)₄N(CH₂CH₂)₂NC₆₀}_n•nC₆₀•2nCS₂ (2) at 180 K (CCDC 1016154). C₁₃₄H₂₀N₂O₈Rh₂S₄: *M* = 2119.58, black block, 0.136 × 0.117 × 0.039 mm, λ = 1.54178 Å, orthorhombic, space group *Pnma* (no. 62), *a* = 19.3103(8), *b* = 19.7315(8), *c* = 19.9656(9) Å, *T* = 180(2) K, *V* = 7607.3(6) Å³, *Z* = 4, 84489 reflections measured, 8972 unique (*R*_{int} = 0.1018) which were used in all calculations, Bruker Apex II; 2θ_{max} = 41.32°; min/max

transmission = 0.6684/ 0.7586 (multi-scan absorption correction applied); direct and Patterson methods solution; full-matrix least squares based on F^2 (SHELXT and SHELXL-2012); The final $wR(F_2)$ was 0.2605 (all data), conventional $R_1 = 0.0837$ computed for 6112 reflections with $I > 2\sigma(I)$ using 535 parameters with 0 restraints.

Crystal data for $\{\text{Rh}_2(\text{O}_2\text{CCH}_3)_4\text{N}(\text{CH}_2\text{CH}_2)_2\text{NC}_{60}\}_n \cdot n\text{C}_{60} \cdot 2n\text{CS}_2$ (2) at 296 K (CCDC 1016155). $\text{C}_{134}\text{H}_{20}\text{N}_2\text{O}_8\text{Rh}_2\text{S}_4$: $M = 2119.58$, black block, $0.136 \times 0.117 \times 0.039$ mm, $\lambda = 1.54178$ Å, orthorhombic, space group $Pnma$ (no. 62), $a = 19.3895(10)$, $b = 19.8056(10)$, $c = 20.0289(10)$ Å, $T = 296(2)$ K, $V = 7691.5(7)$ Å³, $Z = 4$, 85351 reflections measured, 9074 unique ($R_{\text{int}} = 0.0947$) which were used in all calculations, Bruker Apex II; $2\theta_{\text{max}} = 41.16^\circ$; min/max transmission = 0.6602/ 0.7456 (multi-scan absorption correction applied); direct and Patterson methods solution; full-matrix least squares based on F^2 (SHELXT and SHELXL-2012); The final $wR(F_2)$ was 0.2898 (all data), conventional $R_1 = 0.0886$ computed for 5848 reflections with $I > 2\sigma(I)$ using 521 parameters with 0 restraints.

Crystal data for $\{\text{Rh}_2(\text{O}_2\text{CCH}_3)_4\text{N}(\text{CH}_2\text{CH}_2)_2\text{NC}_{60}\}_n \cdot n\text{C}_{70} \cdot n\text{CS}_2$ (3) at 90 K (CCDC 1016157). $\text{C}_{143}\text{H}_{20}\text{N}_2\text{O}_8\text{Rh}_2\text{S}_2$: $M = 2163.55$, black block, $0.340 \times 0.200 \times 0.190$ mm, $\lambda = 1.54178$ Å, orthorhombic, space group $Pmma$ (no. 51), $a = 19.6991(18)$, $b = 15.8057(15)$, $c = 12.8041(12)$ Å, $V = 3986.7(6)$ Å³, $Z = 2$, 44223 reflections measured, 4195 unique ($R_{\text{int}} = 0.0812$) which were used in all calculations, Bruker Apex DUO; $2\theta_{\text{max}} = 136.83^\circ$; min/max transmission = 0.674/0.745 (multi-scan absorption correction applied); direct and Patterson methods solution; full-matrix least squares based on F^2 (SHELXT and SHELXL-2014/7); The final $wR(F_2)$ was 0.3567 (all data), conventional $R_1 = 0.1133$ computed for 3431 reflections with $I > 2\sigma(I)$ using 298 parameters with 113 restraints.