**Supplementary Information for**

# Guest-Induced Diverse Self-Assembles of an Oligopyrrole

YichengFang, Huiqi Wei, Caixia Li, Gen Liu, Fan Wang, Lamei Wu, Zhengxi Huang*, Xi Chen*
Zhan Zhang*

Key Laboratory of Catalysis and Energy Materials Chemistry of Ministry of Education & Hubei Key Laboratory of Catalysis and Materials Science, College of Chemistry & Materials Science, South-Central Minzu University, Wuhan 430073, China.

## 1. X-Ray experimental

**Bromide-SOF** (CCDC No.: 2393850)

Crystals grew as red plates upon the slow evaporation of a DCE/hexanes solution of **1** with excess of TEABr or HBr. The data crystal had approximate dimensions of 0.12 x 0.06 x 0.05 mm. All measurements were made on a Bruker D8 Venture diffractometer with graphite monochromated Ga-K radiation. The data were collected at a temperature of 200 K. Of the 151081 reflections that were collected, 19358 were unique ($R_{int}$ = 0.1031). Data were collected and integrated using the Bruker SAINT software package. The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically. All refinements were performed using the SHELXTL crystallographic software package Bruker-AXS.

**Table S1. Crystal data for bromide-SOF.**

| | | |
|---|---|---|
| Empirical Formula | | $C_{131}H_{180}BrF_6N_{18}O_{18}S_2$ |
| Formula Weight | | 2552.95 |
| Temperature | | 200 K |
| Crystal Color, Habit | | red, plate |
| Crystal Dimensions | | 0.12 X 0.06 X 0.05 mm |
| Crystal System | | Triclinic |
| Space Group | | *P-1* |
| Lattice Parameters | *a*/Å | 19.2799(14) |
| | *b*/Å | 21.1893(16) |
| | *c*/Å | 24.3397(17) |
| | *α*/deg | 94.007(4) |
| | *β*/deg | 95.264(3) |
| | *γ*/deg | 110.225(3) |
| | V/Å$^3$ | 9235.9(12) |
| *Z* Value | | 2 |
| $D_{calc}$/g cm$^{-3}$ | | 0.918 |
| $F_{000}$ | | 2714.0 |
| No. of Reflections Measured | Total: | 151081 |
| | Unique: | 19358 ($R_{int}$ = 0.1031) |
| Data/restraints/parameters | | 19358/131/1658 |
| *R1*; *wR2* (all data) | | 0.1080; 0.2649 |
| Goodness of Fit Indicator (GOF) | | 1.071 |
| *R1*; *wR2* (I>2σ(*I*)) | | 0.0791; 0.2442 |

**Iodide-SOF** (CCDC No.: 2393851)

Crystals grew as red blocks upon the slow diffusion of DCE/hexanes solution of **1** with excess of TEAI. The data crystal had approximate dimensions of 0.13 x 0.12 x 0.10 mm. All measurements were made on a D8 Venture diffractometer with graphite monochromated Ga-K radiation. The data were collected at a temperature of 100 K. Of the 167212 reflections that were collected, 20405 were unique ($R_{int}$ = 0.0737). Data were collected and integrated using the Bruker SAINT software package. The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically. All refinements were performed using the SHELXTL crystallographic software package Bruker-AXS.

**Table S2. Crystal data for iodide-SOF.**

| | | |
|---|---|---|
| Empirical Formula | | $C_{131}H_{180}F_6IN_{18}O_{18}S_2$ |
| Formula Weight | | 2599.94 |
| Temperature | | 100 K |
| Crystal Color, Habit | | red, block |
| Crystal Dimensions | | 0.13 X 0.12 X 0.10 mm |
| Crystal System | | Triclinic |
| Space Group | | *P-1* |
| Lattice Parameters | *a*/Å | 18.9098(11) |
| | *b*/Å | 20.9683(11) |
| | *c*/Å | 23.7373(15) |
| | *α*/deg | 96.441(2) |
| | *β*/deg | 97.288(3) |
| | *γ*/deg | 112.541(2) |
| | V/Å$^3$ | 8488.9(9) |
| *Z* Value | | 2 |
| $D_{calc}$/g cm$^{-3}$ | | 1.017 |
| $F_{000}$ | | 2750 |
| No. of Reflections Measured | Total: | 167212 |
| | Unique: | 20405 ($R_{int}$ = 0.0737) |
| Data/restraints/parameters | | 20405/147/1718 |
| *R1*; *wR2* (all data) | | 0.0995; 0.2246 |
| Goodness of Fit Indicator (GOF) | | 1.042 |
| *R1*; *wR2* (I>2σ(*I*)) | | 0.0773; 0.2087 |

**[1•1⊂(EA)$_2$]** (CCDC No.: 2489940)

Crystals grew as red plates upon the slow diffusion of hexanes into an ethyl acetate solution of **1**. The data crystal had approximate dimensions of 0.16 x 0.06 x 0.05 mm. All measurements were made on a Bruker D8 Venture diffractometer with graphite monochromated Ga-K radiation. The data were collected at a temperature of 100 K. Of the 112355 reflections that were collected, 19654 were unique ($R_{int}$ = 0.1299). Data were collected and integrated using the Bruker SAINT software package. The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically. All refinements were performed using the SHELXTL crystallographic software package Bruker-AXS.

**Table S3. Crystal data for [1•1⊂(EA)$_2$].**

| | | |
|---|---|---|
| Empirical Formula | | $C_{48}H_{66}F_3N_6O_9S$ |
| Formula Weight | | 960.12 |
| Temperature | | 100 K |
| Crystal Color, Habit | | red, plate |
| Crystal Dimensions | | 0.16 X 0.06 X 0.05 mm |
| Crystal System | | Triclinic |
| Space Group | | *P-1* |
| Lattice Parameters | *a*/Å | 15.4821(4) |
| | *b*/Å | 17.588(4) |
| | *c*/Å | 23.232(6) |
| | *α*/deg | 73.270(11) |
| | *β*/deg | 74.936(10) |
| | *γ*/deg | 77.737(10) |
| | V/Å$^3$ | 5785(2) |
| *Z* Value | | 4 |
| $D_{calc}$/g cm$^{-3}$ | | 1.102 |
| $F_{000}$ | | 2044 |
| No. of Reflections Measured | Total: | 112355 |
| | Unique: | 19654 ($R_{int}$ = 0.1299) |
| Data/restraints/parameters | | 19654/35/1319 |
| *R1*; *wR2* (all data) | | 0.1186; 0.2904 |
| Goodness of Fit Indicator (GOF) | | 1.110 |
| *R1*; *wR2* (I>2σ(*I*)) | | 0.1011; 0.2763 |

**Zig-zag-polymer** (CCDC No.: 2489938)

Crystals grew as yellow blocks upon the slow diffusion of diethyl ether into a DCM solution of **1**. The data crystal had approximate dimensions of 0.12 x 0.10 x 0.10 mm. All measurements were made on a Bruker D8 Venture diffractometer with graphite monochromated Ga-K radiation. The data were collected at a temperature of 100 K. Of the 175485 reflections that were collected, 25763 were unique ($R_{int}$ = 0.1190). Data were collected and integrated using the Bruker SAINT software package. The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically. All refinements were performed using the SHELXTL crystallographic software package Bruker-AXS.

**Table S4. Crystal data for zig-zag-polymer.**

| | | |
|---|---|---|
| Empirical Formula | | $C_{148}H_{217}F_9N_{18}O_{25}S3$ |
| Formula Weight | | 2915.56 |
| Temperature | | 100 K |
| Crystal Color, Habit | | yellow, block |
| Crystal Dimensions | | 0.12 X 0.10 X 0.10 mm |
| Crystal System | | Monoclinic |
| Space Group | | $P2_1/c$ |
| Lattice Parameters | $a$/Å | 31.193(3) |
| | $b$/Å | 13.3642(13) |
| | $c$/Å | 42.964(5) |
| | $\alpha$/deg | 90 |
| | $\beta$/deg | 110.582(4) |
| | $\gamma$/deg | 90 |
| | V/Å$^3$ | 16766(3) |
| $Z$ Value | | 4 |
| $D_{calc}$/g cm$^{-3}$ | | 1.155 |
| $F_{000}$ | | 624 |
| No. of Reflections Measured | Total: | 175485 |
| | Unique: | 25763 ($R_{int}$ = 0.1190) |
| Data/restraints/parameters | | 25763/220/2191 |
| *R1*; *wR2* (all data) | | 0.1397; 0.2874 |
| Goodness of Fit Indicator (GOF) | | 1.035 |
| *R1*; *wR2* (I>2σ(*I*)) | | 0.0878; 0.2469 |

**Interlocked-polymer** (CCDC No.: 2517738)

Crystals grew as red blocks through the slow evaporation of a DCM/methanol solution of **1**. The data crystal had approximate dimensions of 0.10 x 0.06 x 0.05 mm. All measurements were made on a Bruker D8 Venture diffractometer with graphite monochromated Ga-K radiation. The data were collected at a temperature of 100 K. Of the 46599 reflections that were collected, 8014 were unique ($R_{int}$ = 0.0669). Data were collected and integrated using the Bruker SAINT software package. The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically. All refinements were performed using the SHELXTL crystallographic software package Bruker-AXS.

**Table S5. Crystal data for interlocked-polymer.**

| | | |
|---|---|---|
| Empirical Formula | | $C_{45}H_{63}F_3N_6O_8S$ |
| Formula Weight | | 905.07 |
| Temperature | | 100 K |
| Crystal Color, Habit | | red, block |
| Crystal Dimensions | | 0.10 X 0.06 X 0.05 mm |
| Crystal System | | Triclinic |
| Space Group | | *P-1* |
| Lattice Parameters | *a*/Å | 11.0234(7) |
| | *b*/Å | 14.6125(10) |
| | *c*/Å | 15.6272(10) |
| | *α*/deg | 107.660(3) |
| | *β*/deg | 97.768(3) |
| | *γ*/deg | 90.951(3) |
| | V/Å$^3$ | 2372.2(3) |
| *Z* Value | | 2 |
| $D_{calc}$/g cm$^{-3}$ | | 1.267 |
| $F_{000}$ | | 964 |
| No. of Reflections Measured | Total: | 46599 |
| | Unique: | 8014 ($R_{int}$ = 0.0669) |
| Data/restraints/parameters | | 8014/327/640 |
| *R1*; *wR2* (all data) | | 0.1164; 0.2573 |
| Goodness of Fit Indicator (GOF) | | 1.192 |
| *R1*; *wR2* (I>2σ(*I*)) | | 0.1049; 0.2529 |

**Interlocked-polymer** (CCDC No.: 2489939)

Crystals grew as yellow blocks upon the slow diffusion of hexanes into a DCM solution of **1**. The data crystal had approximate dimensions of 0.12 x 0.10 x 0.10 mm. All measurements were made on a Bruker APEX-II CCD diffractometer with graphite monochromated Mo-K radiation. The data were collected at a temperature of 100 K. Of the 69396 reflections that were collected, 9560 were unique ($R_{int}$ = 0.0989). Data were collected and integrated using the Bruker SAINT software package. The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically. All refinements were performed using the SHELXTL crystallographic software package Bruker-AXS.

**Table S6. Crystal data for interlocked-polymer.**

| | | |
|---|---|---|
| Empirical Formula | | $C_{44}H_{59}F_3N_6O_7S$ |
| Formula Weight | | 873.03 |
| Temperature | | 100 K |
| Crystal Color, Habit | | yellow, block |
| Crystal Dimensions | | 0.12 X 0.10 X 0.10 mm |
| Crystal System | | Triclinic |
| Space Group | | *P-1* |
| Lattice Parameters | *a*/Å | 17.5583(16) |
| | *b*/Å | 17.8234(17) |
| | *c*/Å | 20.4700(17) |
| | *α*/deg | 95.950(4) |
| | *β*/deg | 92.330(4) |
| | *γ*/deg | 102.751(4) |
| | V/Å$^3$ | 6201.1(10) |
| *Z* Value | | 4 |
| $D_{calc}$/g cm$^{-3}$ | | 0.935 |
| $F_{000}$ | | 1856 |
| No. of Reflections Measured | Total: | 69396 |
| | Unique: | 9560 ($R_{int}$ = 0.0989) |
| Data/restraints/parameters | | 9560/2162/1283 |
| *R1*; *wR2* (all data) | | 0.1415; 0.3676 |
| Goodness of Fit Indicator (GOF) | | 1.499 |
| *R1*; *wR2* (I>2σ(*I*)) | | 0.1184; 0. 3430 |

## 2. Calculations

All density functional theory (DFT) calculations were performed using the Gaussian 16 software package[1] on a local Linux cluster. Geometric optimizations were carried out at the B3LYP level of theory using a mixed-basis set: the 6-311G(d,p) basis set was employed for all atoms except iodine (I), for which the SDD basis set was used. Geometric optimizations were carried out at the B3LYP/6-311G** level of theory. Vibrational frequency and Gibbs free energy calculations were conducted at the same level to ensure that the optimized structures corresponded to true local minima on the potential energy surface. Non-covalent interaction (NCI) analysis was performed based on the wavefunctions obtained from the DFT calculations and visualized using the NCIPLOT program[2]. The electrostatic potential (ESP) surfaces were generated by the Multiwfn software[3] using the wavefunctions of the optimized geometries and were subsequently rendered using the VMD (Visual Molecular Dynamics) software[4].

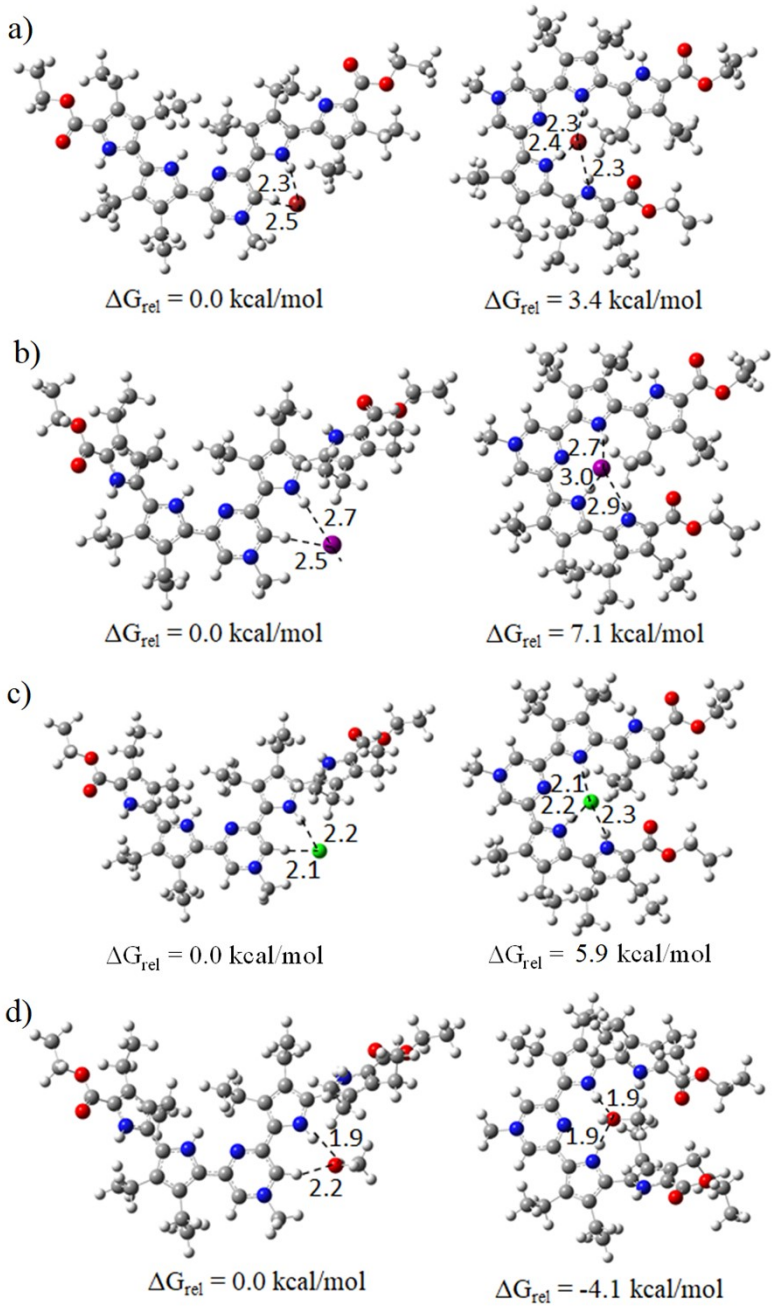


Figure S1. Optimized geometries of bromide (a), iodide(b), chloride (c) and methanol (d) complexes of **1** in twisted (left) and U-shaped (right) conformation. Relative Gibbs free energies ($\Delta G_{rel}$) for the U-shaped complexes are calculated with respect to their corresponding twisted counterparts.

## References

1. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. Gaussian 16 Rev. C.01, Wallingford, CT, 2016.

2. Boto, R. A.; Peccati, F.; Laplaza, R.; Quan, C.; Carbone, A.; Piquemal, J.-P.; Maday, Y.; Contreras-García, J., NCIPLOT4: Fast, Robust, and Quantitative Analysis of Noncovalent Interactions. Journal of Chemical Theory and Computation 2020, 16, 4150-4158.

3. Lu, T., A comprehensive electron wavefunction analysis toolbox for chemists, Multiwfn. The Journal of chemical physics 2024, 161, 082503.

4. Humphrey, W.; Dalke, A.; Schulten, K., VMD: visual molecular dynamics. Journal of molecular graphics 1996, 14, 33-8, 27-8.