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Photochromic Rhenium-Based Molecular Rectangles: Syntheses, Structures, Photophysical Properties, and Electrochemistry

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ABSTRACT: Two novel *fac*-Re(CO)₃-based rectangles {[(CO)₃Re- $(\mu$ -Cl)₂Re(CO)₃]₂ $(\mu$ -L)₂} (1) and {[(CO)₃Re $(\mu$ -OC₄H₉)₂Re-(CO)₃]₂ $(\mu$ -L)₂}(2) based on new photochromic dithienylethene-containing ligand 2,7-di(pyridin-4-yl)-9,10-bis(5-chloro-2-methyl-thien-3-yl)-phenanthrene (L) were prepared. They displayed varying photochromic properties both in solution and in the single-crystal state. Through a judicious choice of the bridging ligands along the short sides of the rectangles, the photophysical and electrochemical properties of the complexes could also be readily tuned.



SUPPORTING Information

INTRODUCTION

Over the last two decades, much attention has been paid to fac- $Re(CO)_3$ -based supramolecules that are assembled from 4,4'bipyridyl ligands and display discrete two- and three-dimensional structures owing to their application prospects in the fields of host-guest chemistry, photocatalysis, bioactivity, and functional molecular devices. ⁷ This continuing interest is evidenced by numerous fac-Re(CO)₃-based supramolecular assemblies such as triangles, rectangles, squares, prisms, and so on. For example, Hupp, Lu, and other groups have prepared a series of rectangular tetrarhenium molecules. Some of the Re(I) rectangles feature alternating pyrazine and 4,4'-bpy edges.^{8,9} Some of the Re(I) rectangles have thiolates,^{10,11} alkoxides,¹² or 2,2'-bisbenzimidazolate^{13–16} and chloranilic acid¹⁷ hydroxyl group¹⁸ along the short edges as the bridging ligands and rigid or semirigid 4,4'-bpy linkers along the other two edges. Lees^{19,20} and Lin²¹ reported a number of luminescent square molecules $[ClRe(CO)_3(\mu-4,4'-bpy)]_4$. Some of these Re-based assemblies have been demonstrated to exhibit sensing properties for volatile molecules.^{13,17,20} However, to the best of our knowledge, there have been no examples of rhenium metallocycles incorporating a photoswitching ligand reported to date. Tunable Re-based metallocycles that incorporate a switching ligand are potentially useful in optoelectronics as well as in chemical reactivity. It is well known that switching molecules would be able to modulate the chemophysical properties of molecular devices because they can interconvert between two thermally stable forms when irradiated with UV and visible light.²² In this regard, photoresponsive 1,2-dithienylethene (DTE) derivatives are particularly attractive due to the dramatic steric and electronic differences between the photosensitive isomers and display promising application prospects in optical memory and switches.²³⁻³⁰ Here, we report the design and syntheses of two photoresponsive rectangular tetrarhenium molecules based

on new photochromic dithienylethene-containing 4,4'-bipyridyl ligand 2,7-di(pyridin-4-yl)-9,10-bis(5-chloro-2-methylthien-3-yl)-phenanthrene. The photochromism of the new molecules is preliminarily investigated by electronic absorption and emission spectroscopy and cyclic voltammetry.

RESULTS AND DISCUSSION

Synthesis of Ligand L. The synthesis route to the new photochromic ligand is shown in Scheme 2. The characterization of L and its intermediates S3 and S4 was accomplished via the ¹H NMR spectrum, IR spectrum, and elemental analysis. The ¹H NMR spectrum of L shows two signals for the methyl groups (δ , 2.09 and 2.04 ppm) and the protons located on the thiophene rings (δ , 6.60 and 6.56 ppm) as well as two signals for the protons located on the phenanthrene ring (δ_i 7.90 and 7.86 ppm) (Figure S1). Irradiation with 313 nm UV light led to the appearance of a third signal (δ , 2.69 and 2.70 ppm for the methyl group and 7.05 ppm for the thiophene ring) belonging to the closed form (Scheme 2). According to the signal integrals before and after irridiation, the peaks at 2.09, 6.56, and 7.86 ppm should be assigned to the parallel isomer and the peaks at 2.04, 6.60, and 7.90 ppm should be attributed to the antiparallel isomer. This observation is similar to that of previously reported 9,10-bis-[5-phenyl-2-methylthien-3-yl]-phenanthrene in Walko's paper.³¹ The solution simultaneously changed from colorless to red-purple. After irradiation for 20 min, the closed form of L accounted for

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Scheme 1. Synthesis Route to New Photochromic Ligand L^a



"Reagents and conditions: (i) K₂CrO₇, H₂SO₄, AcOH, H₂O. (ii) (1) SOCl₂; (2) AlCl₃, CH₂Cl₂, 2-chloro-5-methylthiophene. (iii) TiCl₄, Zn, THF, reflux. (iv) 4-Pyridyl boronic acid, Pd(PPh₃)₄, K₂CO₃(aq), reflux.





about 12% of the total. The low photocyclization conversion might be related to the absence of donor substituents or a conjugated system on the thiophene rings,³² Additionally, single crystals of L, grown by slow evaporation from ethyl acetate were analyzed by X-ray diffraction (Figure 1). There



Figure 1. ORTEP representation of L with 30% thermal ellipsoids.

are two molecules in the unit cell, and the distance between two pyridyl N atoms is ca. 15.6 Å. In the crystal structure, L adopts an antiparallel (racemic) configuration, as Fraysse and co-workers observed for the related perfluoro-1,2-bis(2-iodo-5methylthien-4-yl)cyclopentene.³³ This conformation is adapted for the cyclization reaction that can occur with relatively small movements. Irradiating the single crystals of L with 313 nm UV light resulted in an apparent color change from colorless to red-purple, which indicated that photocyclization also occurred in the single-crystal state. Thus, a rigid ditopic linker suitable for the fabrication of light-responsive MOFs was obtained by incorporating 4-pyridyl groups on the phenanthrene units. As we know, the 4,4'-bipyridyl linker is one of the most versatile building units for constructing discrete and polymeric MOFs. The Suzuki coupling reaction of the 2,7positions of the phenanthrene unit affords efficient synthesis strategies for the design of photochromic ligands because this would lead to many other rigid ditopic linkers with carboxylate and amino binding groups suitable for photoresponsive MOFs.

Self-Assembly and Characterizations of Molecular Rectangles. Chloride-bridged molecular rectangle $\{[(CO)_3Re(\mu-Cl)_2Re(CO)_3]_2(\mu-L)_2\}$ (1) was obtained unexpectedly by reacting $Re_2(CO)_{10}$, ligand L, and chloroanilic acid (H₂CA) in a toluene-acetone mixture in the dark and separated as yellow-brown crystals (Scheme 3). When $Re_2(CO)_{10}$ was treated with L in 1-butanol in the dark, butoxy-bridged rectangle $\{[(CO)_3Re(\mu-OC_4H_9)_2Re(CO)_3]_2(\mu-L)_2\}$ (2) was obtained as yellow crystals. These two compounds are air- and moisture-stable. Complex 1 is soluble in very polar solvents such as N,N'-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) but not soluble in dichloromethane, chloroform, acetone, and tetrahydrofuran. Complex 2 is soluble in DMSO.

Single crystals of 1 and 2 were studied by an X-ray diffraction technique. The ORTEP diagrams of 1 and 2 (Figures 2 and 3) revealed a similar rectangular structural motif, where two planar ligands were coordinated to four rhenium atoms that were bridged by four chloride atoms or by four butoxyl groups. Four Re atoms are located at the four corners of a rectangle. Each metal center is coordinated to one $N_{pyridyl}$ atom of ligand L, two chloride/oxygen atoms, and three C atoms of C≡O groups. Two face-to-face pyridine rings are almost parallel, and the dihedral angles between them are 1.205° (for 1) and 4.537° (for 2), respectively. Two phenanthrene planes are antiparallel, and the dihedral angles between them are nearly 0° (for 1) and 2.948° (for 2), respectively. The centroid-centroid distances between two pyridine units are ~3.75 Å (for 1) and ~3.55 Å (for 2), and the distances between two pairs of parallel benzene rings on the phenanthrene units are \sim 3.67 Å (for 1) and 3.63 Å (for 2), suggesting strong $\pi \cdots \pi$ stacking interactions between two ligands. Further comparison of the two structures showed that the sizes of rectangles 1 (ca. 20.126 \times 3.794 Å²) and 2 (ca. $20.172 \times 3.379 \text{ Å}^2$) measured from the rhenium centers are also different, where the short sides of 2 decreased by 0.41 Å compared to those of 1 due to the smaller oxygen bridges. Both structures give rise to strong crystallographic disorder of

Article

Scheme 3. Synthesis Routes to New Molecular Rectangles 1 and 2



Figure 2. ORTEP plot of rectangle 1 with hydrogens excluded for clarity. Thermal ellipsoids are drawn to 50% probability.

the 5-chloro-2-methylthiophene groups probably due to the coexistence of two parallel and antiparallel isomers.

There exist three characteristic bands of fac-Re(CO)₃ at 2043, 2026, and 1907 cm⁻¹ in the IR spectrum of **1**, while the IR spectrum of **2** showed bands at 2020, 2006, and 1889 cm⁻¹, shifted ca. 20 cm⁻¹ in the carbonyl stretching frequencies (Figures S3 and S4). On the basis of the above studies, it showed that the subtle geometric and electronic structures of the two rectangles varied by changing the bridging groups along the shorter sides, which would be expected to have an effect on their photophysical and electrochemical properties.

To verify that no significant framework decomposition occurred during solvation, a sample of crystal 1 was dissolved in DMSO- d_6 , analyzed by ¹H NMR spectroscopy, and compared with the proton spectrum of ligand L (Figure S5). As the spectrum of the open form of 1 shows, there are two sets of doublet peaks at 8.87 and 7.95 ppm that could be assigned to H_{α} and H_{β} on pyridyl rings. The downfield chemical shifts (0.19 and 0.28 ppm) of protons on pyridyl rings should indicate that the coordination is retained in

solution. The doublets at 9.28 and 8.28 ppm and the singlet at 7.89 could be assigned to the protons on the phenanthrene units. The two singlet peaks at 6.99 and 6.82 ppm could be attributed to the protons on thiophene rings, and the peaks at 2.09 and 2.03 ppm could be assigned to methyl groups on thiophene rings, indicating that there exist parallel (photochemically inactive) and antiparallel (photochemically active) isomers of ligand in rectangle 1. This spectrum showed a highly symmetrical species, consistent with the rectangular crystal structure. By comparison, it is found that the protons on phenanthrene units in 1 all shifted downfield relative to those in ligand L. We concluded that the framework remained intact throughout the solvation process. The photochromic reaction of the rectangle was also monitored by ¹H NMR spectra (Figures 4 and S6). When irradiated with 365 nm light, the nearly colorless solution turned red-purple, the spectrum showed that the signals at 6.82 and 2.09 ppm decreased to almost zero, and the new signals at 7.44 and 2.61 ppm belonging to the closed forms of the complex appeared. This observation indicated that the ditopic 4,4'-pyridyl ligand



Figure 3. ORTEP plot of rectangle 2 with hydrogens excluded for clarity. Thermal ellipsoids are drawn to 30% probability.



Figure 4. ¹H NMR (400 MHz) of 1 in DMSO- d_6 before and after irradiation at 365 nm (left) and the color changes in the solution and crystal. The signals corresponding to the antiparallel (\bullet) and parallel (\bullet) conformations of the open form and the closed form (\star) are labeled.

maintained photochromic activity when incorporated into a tetrarhenium rectangle. The relative integration of the new signals showed that a photostationary state was reached after irradiation for 50 min, and the concentration of the closed form of **1** reached ca. 35% of the total.

In the single-crystal state, the Re(I) rectangles also underwent photocyclization, which was verified by the fact that irradiating single crystals of 1 and 2 with 365 nm light resulted in apparent changes in the crystal color (for 1, yellowbrown to red-purple; for 2, yellow to red-brown) (Figures 4 and S7). However, X-ray diffraction experiments based on the fully irradiated crystals showed only the presence of the openform structure of the complex, which was likely due to the low conversion to the closed form. Although the photochromism of Re(I) complexes 1 and 2 was fully reversible in solution (the red solutions of the closed photoproduct returned to the initial yellow state upon irradiation with >500 nm visible light), their crystals did not completely go back to their initial state when irradiated with visible light. After more than 2 h of irradiation with visible light, the red coloration did not change much, probably because the local chemical environment in the solid

state was suppressing the ring-opening reaction, as observed in other dithienylethene- or azobenzene-derivatized MOFs.^{34,35}

Electronic Absorption and Emission Spectroscopy. UV-vis absorption maxima and corresponding molar absorption coefficients of L, 1, and 2 are listed in Table 1.

The photochromic behavior of L was studied by irradiation with UV light at selected wavelengths and monitored by UV– vis spectroscopy. The absorption maxima of the open form appeared at wavelengths of 221 and 288 nm corresponding to

Table 1. Major Absorptions in the UV–Vis Spectra of L, 1, and 2 before and after Irradiation^a

compound	open form	photostationary state
L	221 (39.7); 288 (76.6)	258 (38.2); 303 (70.4); 338 (52.0); 544 (3.4); 584 (2.9)
1	293 (73.3); 338(62.6)	327(82.9); 549 (4.2); 588 (3.7)
2	295(94.4); 333(64.2)	310(84.0);; 545(2.7); 560(2.0)

^{*a*}The values correspond to λ_{max} (nm), and values in parentheses correspond to ε (× 10³ cm⁻¹ M⁻¹) measured in methanol or DMF.



Figure 5. (a) UV–vis absorption and (b) emission spectral changes of L (1.30×10^{-5} M in MeOH) (λ_{ex}^{max} = 341 nm at 298 K) upon irradiation at 313 nm.



Figure 6. (a, c) UV-vis absorption and (b, d) emission spectral changes of 1 (1.30×10^{-5} M) and 2 (1.20×10^{-5} M) in DMF using excitation wavelengths of 345 and 366 nm, respectively, at 298 K upon irradiation at 365 nm.

 $n-\pi^*$ and $\pi-\pi^*$ transitions of the 2,7-di(4-pyridyl)-phenanthrene moiety and the thiophene moiety. Upon irradiation at a wavelength (313 nm) near their absorption maxima, the colorless solution of L turned to red-purple and the UV-vis spectrum showed one new additional absorption band at ca. 450-630 nm in the visible region. This new absorption band might be assigned as an absorption of the ring-closing isomer, as observed for 9,10-bis-[5-phenyl-2-methylthien-3-yl]-phenanthrene³¹ in Walko's paper. (Table 1 and Figure 5). The photostationary state was reached after exposure to UV light for ca. 10 min. Irradiation with visible light (>500 nm) resulted in a photochemical ring-opening process and the restoration of the original spectrum of L, showing the good reversibility of the ligand (Figure S8).

In the ring-open isomer of **L**, fluorescence intensity was observed at 402 and 417 nm when excited at $\lambda_{ex}^{max} = 341$ nm (Figure 5b). After a solution of **L** was irradiated at 313 nm, the fluorescence intensity at 402 nm decreased to almost zero. The original emission spectrum was regenerated when the colored

solution was irradiated with light of $\lambda > 500$ nm. Thus, the reversible interconversion between the open form and closed form modulates the intensity of the emitted light at this particular wavelength.

The UV-vis absorption spectra of 1 and 2 in DMF showed two absorption bands at ca. 293, 338 nm and 295, 333 nm, respectively, which were largely red shifted in comparison to the free-ligand bands, which are assigned to a ligand-centered $\pi-\pi^*$ transition in the high-energy region and a metal-toligand charge transfer (MLCT) $[d\pi(\text{Re})-\pi^*(\text{L})]$ transition in the low-energy region, ^{3,20,36} respectively. Upon irradiation, the light yellow-brown solution of complex 1 changed to redpurple and the yellow solution of complex 2 changed to red. The photostationary states of the solution of complexes of 1 and 2 were reached after exposure to 365 nm for about 3 min (for 1) and 30 s (for 2), showing a faster photocyclization conversion compared to that of the free ligand. The UV-vis absorption spectra showed that two sets of new absorption bands were generated at ca. 327, 549, and 588 nm and 310, 545, 560 nm, respectively, after irradiation. These new absorption bands were assigned as metal-perturbed IL transitions of the ring-closing isomers of the rectangles, which were mixed with MLCT transitions in the low-energy region, as observed for $Zn_4O(TPDC)_3$ [TPDC = 9,10-bis(2,5dimethylthiophen-3-yl)-phenanthrene-2,7-dicarboxylate]³⁴ in Patel's paper and some other coordination compounds with photochromic ligands.²⁴ The extent of π -conjugation in the closed forms of rectangles 1 and 2 would be expanded upon photocyclization. Figure 6a,c shows the UV-vis absorption spectral changes of complexes 1 and 2 in solution. Irradiation with visible light (>500 nm) resulted in a photochemical ringopening process, and the original spectra of 1 and 2 were restored, showing the good reversibility of the complexes (Figure S9).

Excitation into either the intraligand (IL) or MLCT band of the open form of complexes 1 ($\lambda_{ex}^{max} = 345 \text{ nm}$) and 2 (λ_{ex}^{max} = 366 nm) in DMF resulted in broad emissions with maxima at 550 and 592 nm, respectively. Upon irradiation with 365 nm light in the open forms of complexes 1 and 2, the emission intensities at ca. 550 and 592 nm were found to decrease and the emission maxima were blue-shifted. Emission spectral changes of 1 and 2 are shown in Figure 7b,d. According to the spectroscopic studies on previously reported fac-Re(CO)₃pyridyl complexes, 36 the emission of 1 and 2 could be assigned as ³MLCT $[d\pi(Re) - \pi^*(L)]$ phosphorescence.

Electrochemical Studies. The cyclic voltammetry (CV) scan of L displayed three quasireversible reduction couples (Figure 7a). The first two reduction couples at -1.73 and -1.94 V (vs SCE) overlap to some extent and could be assigned to thiophene-based reduction, according to previous electrochemical studies on another related dithienylethene compound.³⁷ The reduction couples at -2.57 V (vs SCE) are ascribed to pyridine-based reduction. The first two reductions are one-electron events. On conversion to the closed form, two new irreversible reduction waves, which also partially overlap, were observed at less negative potentials (-1.18 and -1.34 V)vs SCE). This observation confirms the thiophene-based reduction because conversion of the thiophene rings in the open form to the condensed thiophene units has more π conjugation and hence a better π -accepting ability, which would be expected to lead to less negative potentials.

The CV curve of 1 is shown in Figure 7b. There are two overlapping reduction couples near -1.41 V and one irreversible oxidation wave at +1.57 V. When the negative potential limit is set to -3.0 V, the CV curve shows another reduction couple at -2.49 V and another irreversible oxidation wave at +1.22. By comparison with the CV curve of the ligand, the oxidation at +1.22 V may be ascribed to the ligandcentered oxidation while the irreversible oxidation waves at +1.57 V can be assigned as the oxidation of Re^{I} to Re^{II} , according to the electrochemical studies of other $Re(CO)_{3}$ based complexes.¹⁹ The first overlapping reversible reduction couple at -1.41 V is assigned as two closely spaced oneelectron thiophene-based reductions, which are less negative compared to that of the free ligand. The second reduction couple at -2.49 V is ascribed to pyridine-based reduction, which is more negative compared to that of the ligand. On conversion to the closed form, one new irreversible reduction wave at a less negative potential (-1.05 vs SCE) was observed. This observation confirms the thiophene-based reduction. There were no observable changes for the irreversible oxidation wave for the Re(I) center. The CV studies show



Figure 7. Cyclic voltammograms of (a) L, (b) 1, and (c) 2 before (black solid and dashed lines) and after (blue lines) irradiation with 313 or 365 nm UV light in DMF (0.1 M ⁿBu₄NPF₆). Scan rate: 100 mV s^{-1} .

that in 1 the thiophene-based reduction potentials are 0.32 V less negative than those observed for free ligands. This observation indicates that the coordination of the ligand to the Re₂Cl₂ cluster stabilizes the π^* level in the ligand and lowers the energy of the π^* orbital. The greater overlap of the thiophene-based reductions in 1 compared to that in the free ligand implied a smaller electronic energy gap on coordination to the Re₂Cl₂ cluster center.

Rectangle 2 in DMF showed two distinct sets of reversible reduction couples, one quasireversible reduction wave, and two oxidation waves (Figure 7c). The first two reversible reduction couples at -1.36 and -1.84 V, two one-electron events, can be assigned to thiophene-based reduction, and the third quasireversible reduction wave at -2.64 V can be assigned to

pyridine-based reduction. The irreversible oxidation waves at +1.50 V may be attributed to the oxidation of the metal centers. Similarly, one new irreversible reduction at a less negative potential (-1.01 vs SCE) was also observed for 2 upon photocyclization.

The CV studies show that in both 1 and 2 the thiophenebased reduction potentials are much less negative than those observed for the free ligand. The coordination of the ligand to the metal usually stabilizes the π^* level in the ligand and lowers the energy of the π^* orbital. The greater overlap of the thiophene-based reductions in 1 compared to that in free ligand implies a smaller electronic energy gap on coordination to the Re₂Cl₂ cluster center, and the greater separation in 2 shows a larger electronic energy gap upon coordination to the Re₂(OBu)₂ cluster center.

CONCLUSIONS

Two photoresponsive rectangular molecules with Re_2Cl_2 and Re_2OBu_2 clusters based on a new photochromic ligand were prepared in this article, and the electrochemical properties of the new compounds were studied. The complexes underwent reversible photochromic reactions in solution and interconverted by irradiation with UV and visible light. The CV studies showed that in 1 and 2 the coordination of the ligand to metal centers resulted in the thiophene-based reduction potentials being less negative than those observed for free ligand, and the photophysical and electrochemical properties were modulated accordingly by irradiation with UV or visible light.

EXPERIMENTAL SECTION

General. ¹H NMR spectra were obtained using a Bruker Avance 400 (400 MHz) or Agilent 600 (600 MHz) spectrometer. Chemical shifts are reported relative to residual solvent signals: CDCl₃: ¹H δ 7.27; DMSO- d_6 : ¹H δ 2.47; CD₂Cl₂: ¹H δ 5.33. The apparent multiplicity is reported as "s" = singlet, "d" = doublet, "dd" = two doublets, "m" = multiplet, "brs" = broad singlet, or "ss" = two singlets. Element analyses were performed on a PerkinElmer model 240C analyzer. Infrared (IR) spectra were obtained in the 400-4000 cm⁻¹ range using a Bio-Rad FTS-40 infrared spectrometer. Photoluminescence spectra were measured on a FLS920 fluorescence spectrophotometer. Emission spectra were collected at 1 nm resolution with an excitation and emission slit width of 3 nm. UVvisible absorbance was measured using a Shimadzu UV mini-1240 spectrophotometer. Cyclic voltammetry and differential pulse voltammetry measurements were performed using a CHI660D (CH Instruments) electrochemical workstation. Electrolyte solutions (0.1 M ⁿBu₄NPF₆) were prepared with dry DMF and degassed with N₂ before use. A platinum-wire counter electrode, a saturated calomel electrode (SCE) as the reference electrode, and a glassy carbon (GC) working electrode were used. All chemicals were of reagent-grade purity or better and used as received. 2,7-Dibromophenanthraquinone (S1)³⁸ 4,4'-dibromobiphenyl-2,2'-dicarboxylic acid (S2)³⁹ 4.4'dibromo-2,2'-bis(5-chloro-2-methylthiophene-3-carbonyl)-biphenyl (S3),³¹ and 2,7-dibromo-9,10-bis(5-chloro-2-methylthien-3-yl)-phenanthrene $(S4)^{31}$ were prepared according to literature methods.

4,4'-Dibromo-2,2'-bis(5-chloro-2-methylthiophene-3-carbonyl)biphenyl (**S3**). $R_f = 0.40$ (petroleum ether/CH₂Cl₂ 2:1); yield 3.2 g (51%); light-yellow solid. ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS, ppm): 7.67 (dd, J = 2 Hz, J = 8 Hz, 2H, Ar–H), 7.49 (d, J = 2 Hz, 2H, Ar–H), 7.26 (dd, J = 2 Hz, J = 8 Hz, 2H, Ar–H), 6.70 (s, 2H, thiophene–H), 2.51 (s, 6H, CH₃). IR (KBr pellet, cm⁻¹): 3081 (w), 2919 (w), 1654 (vs), 1583 (w), 1514 (s), 1454 (s), 1349 (s), 1263 (m), 1230 (vs), 1181 (s), 995 (s), 820 (s). Anal. Calcd for C₂₄H₁₄Br₂Cl₂O₂S₂: C, 45.81; H, 2.24. Found: C, 45.57; H, 2.70.

2,7-Dibromo-9,10-bis(5-chloro-2-methylthien-3-yl)-phenanthrene (S4). $R_f = 0.50$ (petroleum ether/CH₂Cl₂ 2:1); yield 1.5 g (50%); light-yellow solid. ¹H NMR (600 MHz, $CDCl_3$, 25 °C, TMS, ppm): 8.57 (d, *J* = 9 Hz, 2H, Ar–H), 7.78 (d, *J* = 9 Hz, 2H, Ar–H), 7.74 (s, 2H, Ar–H), 6.52 (s, 2H, thiophene–H), 1.99 (s, 6H, CH₃). IR (KBr pellet, cm⁻¹): 2923 (s), 2853 (m), 1654 (w), 1592 (m), 1456 (s), 993 (m), 790 (m). Anal. Calcd for $C_{24}H_{14}Br_2Cl_2S_2$: C, 48.27; H, 2.36. Found: C, 48.22; H, 2.64.

2,7-Di(pyridin-4-yl)-9,10-bis(5-chloro-2-methylthien-3-yl)-phenanthrene (L). S4 (0.90 g, 1.5 mmol), pyridine-4-boronic acid (0.46 g, 3.75 mmol), K_2CO_3 (1.24 g, 9 mmol), and Pd(PPh₃)₄ (104 mg, 0.09 mmol) were added to a degassed mixture of water/EtOH/ toluene (v/v/v = 15/15/10 mL). Then the mixture was refluxed for 24 h under a nitrogen atmosphere. The solvent was removed under vacuum, and the residue was purified by column chromatography (silica gel, ethyl acetate) to yield 0.60 g of a white powder (yield 67%). ¹H NMR (600 MHz, CDCl₃, 25 °C, TMS, ppm): 8.91 (d, *J* = 8.4 Hz, 2H, Ar–H), 8.70 (d, *J* = 4.8 Hz, 4H, Py–H_{α}), 8.00 (d, *J* = 8.4 Hz, 2H, Ar–H), 7.90, 7.86 (ss, 2H, Ar–H), 7.56 (m, 4H, Py–H_{β}), 6.60, 6.56 (ss, 2H, thiophene–H), 2.09, 2.04 (ss, 6H, CH₃). IR (KBr pellet, cm⁻¹): 2925 (w), 1594 (s), 1477 (m), 1384 (w), 807 (s). Anal. Calcd for C₃₄H₂₂Cl₂N₂S₂: C, 68.80; H, 3.74; N, 4.72. Found: C, 69.02; H, 3.64; N, 5.10.

Complex $[Re_2(CO)_6(C_{34}H_{22}Cl_2N_2S_2)(\mu_2-Cl)_2]$ (1). Re₂(CO)₁₀ (13 mg, 0.02 mmol), L (6 mg, 0.01 mmol), chloranilic acid (2 mg, 0.01 mmol), and toluene/acetone (8:1, 7 mL) were sealed in a Teflon flask (20 mL) in a steel bomb. The bomb was heated to 140 °C and kept at this temperature for 70 h and then cooled to 25 °C. Yellow-brown crystals of 1 were isolated by filtration, washed with acetone, and then air-dried in a dark environment. Yield 12 mg (50%). ¹H NMR (600 MHz, DMSO- d_6 , 25 °C, TMS, ppm): 9.27 (d, J = 9 Hz, 4H, Ar–H), 8.87 (d, J = 6 Hz, 8H, Py–H_{α}), 8.27 (d, J = 6 Hz, 4H, Ar–H), 7.93 (m, 8H, Py–H_{β}), 7.86 (s, 4H, Ar–H), 6.98, 6.81 (ss, 4H, thiophene–H), 2.08, 2.02 (dd, J = 3 Hz, 12H, CH₃). IR (KBr pellet, cm⁻¹): 2043 (vs), 2026 (vs), 1907 (vs), 1614 (s), 1477 (w), 1384 (w), 802 (m). Anal. Calcd for C₄₀H₂₂Cl₄N₂O₆Re₂S₂: C, 39.87; H, 1.84; N, 2.32. Found: C, 39.62; H, 2.01; N, 2.46.

Complex $[Re_2(CO)_6(C_{34}H_{22}Cl_2N_2S_2)(\mu_2-OBu^n)_2](^nBuOH)$ (2). Re₂(CO)₁₀ (13 mg, 0.02 mmol), L (6 mg, 0.01 mmol), and 1butanol (8 mL) were used in the preparation of 2, following the above procedure for the preparation of 1. Yield 18 mg (70%), yellow crystals. ¹H NMR (600 MHz, CD₂Cl₂, 25 °C, TMS, ppm): 8.43 (brs, 8H, Py–H_a), 7.75–7.52 (m, 8H, Ar–H), 7.23 (brs, 8H, Py–H_β), 7.22–7.07 (m, 4H, Ar–H), 6.73–6.61 (m, 4H, thiophene–H), 4.43 (brs, 8H, OCH₂CH₂CH₂CH₃), 2.28–1.93 (m, 12H, CH₃), 2.08 (brs, 8H, OCH₂CH₂CH₂CH₃), 1.51 (brs, 8H, OCH₂CH₂CH₂CH₃), 1.14 (brs, 8H, OCH₂CH₂CH₂CH₃). IR (KBr pellet, cm⁻¹): 2020 (vs), 2006 (vs), 1889 (vs), 1613 (s), 1384 (w), 806 (m). Anal. Calcd for C₅₂H₅₀N₂O₉S₂Re₂Cl₂: C, 46.11; H, 3.72; N, 2.07. Found: C, 45.75; H, 3.45; N, 2.10.

ASSOCIATED CONTENT

9 Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c01845.

¹H NMR spectra of ligand L and complex 2; IR spectra of L and complexes 1 and 2; photographs of the color change of 2; switching cycles; and a differential pulse voltammogram (PDF)

Accession Codes

CCDC 2011070–2011072 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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