Photothermal Möbius aromatic metallapentalenofuran and its NIR-responsive copolymer†

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Möbius aromatics are very interesting and rare complexes owing to their brand-new chemistry and interesting properties. In this work, metallapentalenofurans with thiophene groups were easily prepared from the reaction of metallapentalyne, terminal arylalkynes, and water in air. The metallapentalenofuran containing a terthiophene moiety showed a good photothermal effect and was the first photothermal Möbius aromatic complex induced by J-aggregates. This photothermal metallapentalenofuran was chemically modified to carry an olefinic group and then was co-polymerized with oligo-(ethylene glycol) methacrylate to afford a thermo-responsive copolymer, whose phase transition behavior can be triggered by near-infrared radiation at 808 nm. This near-infrared-responsive metal-containing copolymer represents a new stimuli-responsive macromolecule.

Introduction

Coplanar Möbius aromatic organometallic complexes are very interesting and rare complexes owing to their brand-new chemistry in terms of structure and bonding.1–4 Thanks to their highly conjugated system, they are expected to display interesting properties for light harvesting, light emission, energy transfer, etc. For example, we found that the Möbius aromatic complex 1 (Fig. 1) exhibits aggregation-enhanced near-infrared emission (AEE)5 behavior. Complex 2 (Fig. 1) has been reported to display photoacoustic imaging properties when irradiated at 680 nm,6 and complex 3 (Fig. 1) shows excellent photothermal effects when exposed to near-infrared (NIR) radiation at 808 nm.3,6 Moreover, complex 3 was chemically modified to produce the first photothermal metal-containing macromolecule 4 (Fig. 1).7

It is noted that metallopolymers with organometallic building blocks are interesting and valuable materials, since they are expected to display properties of both organometallic and polymeric units.8–10 Metallopolymers have been developed as functional materials11–21 to be applied in the field of catch and release,22 electrodes,23 optics,24 ion capture,25 water purification,26 surface wettabiliy,27 self-healing,28 electrocatalysts,29 or others.30,31 A representative metallopolymer is polyferrocenylsilane, which has been developed as a stimuli responsive...
material/sensor on the basis of its redox active properties and can even grow to a metallosupramolecular polymer via a living crystallization-driven self-assembly. However, metallopolymer displays photothermal properties are rare.

In our continuous efforts to develop new metallaromatic complexes, we have recently reported an easy route for the preparation of α-metallapentalenofurans from the reaction of complex 5 with terminal arylalkynes and water in air (Scheme 1). Compared to air or moisture sensitive organometallic complexes using standard Schlenk techniques, these metallapentalenofurans can be polymerized under very mild conditions in good yield, which motivated us to develop them further into functional materials.

In this work, we report a new photothermal metallapentalenofuran, which is the first photothermal Möbius aromatic complex induced by J-aggregates. This metallaromatic complex was incorporated into a thermoresponsive copolymer, which phase transition can be triggered by an NIR laser at 808 nm. The resulted NIR-responsive metal-containing copolymer represents a new stimuli-responsive macromolecule.

Results and discussion
Synthesis of osmapentalenofurans 8–10 with (oligo)thiophen-5-yl groups

Recently, we have reported the reaction of osmapentalene 5 with terminal arylalkynes and water to afford the first α-metallapentalenofurans (6 and 7). Following this chemistry, a series of metallapentalenofurans (8–10) with thiophen-2-yl or oligothiophen-5-yl groups were easily synthesized by the treatment of osmapentane 5 with different ethynylthiophenes (2-ethynylthiophene, 5-ethyl-2,2′-bithiophene, or 5-ethyl-2,2′:5′,2′-terthiophene) and water at room temperature (RT) for 1 day under an air atmosphere (Scheme 1).

Scheme 1 Preparation of osmapentalenofurans 6–10 from osmapentalene 5 and terminal aryl alkynes.

Complexes 8–10 were characterized by nuclear magnetic resonance (NMR) spectroscopy, high-resolution mass spectra (HRMS), and elemental analysis (EA). Complexes 9 and 10 were also characterized by X-ray diffraction analysis. As shown in Fig. S23† (9) and Fig. 2 (10), the structures of 9 and 10 are similar to that of complex 6 except that they contain 2,2′-bithiophen-5-yl and 2,2′:5′,2′-terthiophen-5-yl moieties. The three fused five-membered rings formed by atoms Os1, O1, and C1–C9 are approximately coplanar, as reflected by the mean deviations from the least-squares plane (0.067 Å for 9 and 0.108 Å for 10). All Os–C bond lengths in the metallacycles (Os1–C1 2.091, Os1–C4 2.138, Os1–C7 2.129 Å for 9 and Os1–C1 2.081, Os1–C4 2.139, Os1–C7 2.115 Å for 10) are in the range of those for reported osmapentalenes (1.926–2.175 Å). The C–C bond lengths (1.348–1.440 Å for 9 and 1.356–1.436 Å for 10) of the three fused five-membered rings are between those of C–C and C=C bond lengths. All the structural features indicate that the metallacycles in complexes 9 and 10 are also delocalized, as in the case of the reported osmapentalenofuran 6.

The NMR data of 8–10 are consistent with the solid-state structure. In particular, the 31P{1H} NMR spectra show two signals: the CPh3 signals appear at 10.75 ppm for 8, 10.79 ppm for 9, and 10.81 ppm for 10, the two equivalent OsPh3 signals appear at −17.38 ppm for 8, −17.41 ppm for 9, and −17.42 ppm for 10. The characteristic OsCH signal appears at 13.75 ppm for 8, 13.72 ppm for 9, and 13.73 ppm for 10. These results confirm that the structures of complexes 8–10 are similar to those of complexes 6 and 7.

UV-Vis-NIR absorption spectra and photothermal properties

The UV-Vis-NIR absorption behavior of these highly conjugated metal-containing polycyclic complexes (7–10) is shown in Fig. 3. In the visible region, the maximum absorption bands of 7–10 are located at 572, 581, 597, and 605 nm, respectively. It is understandable that the red shift of the maximum absorption and the increase of the molar extinction coefficient are related to the increasing number of substituted thiophene units.

To our surprise, complex 10 with the 2,2′:5′,2′-terthiophen-5-yl group was found to exhibit a new broad absorption band...
covering the range of 700–900 nm. Its absorption pattern and intensity are very similar to those of complex 3, which exhibits excellent photothermal behavior. Inspired by this result, we examined the photothermal properties of complex 10 by measuring the temperature of its solution under NIR laser irradiation (808 nm, 1.0 W cm$^{-2}$). As shown in Fig. 4, the temperature of a water–ethanol (1 : 9, v/v) solution of complex 10 quickly increased under 808 nm light irradiation. In particular, the solution containing 1.00 mg mL$^{-1}$ of complex 10 exhibited a rapid temperature increase from 28 to 57 °C within 5 min, while the solvent presented a negligible temperature change under similar conditions. These results suggest that complex 10 displays good photothermal properties. To understand the observed absorption behavior, we performed time-dependent density functional theory (TD-DFT) calculations on complexes 8–10. The main absorption bands dominated by HOMO → LUMO transitions were calculated to appear at 519, 545, and 568 nm for 8, 9, and 10, respectively. The calculation results are consistent with the observed solution absorption behavior in the visible region ($\lambda_m$ = 581 nm for 8, $\lambda_m$ = 597 nm for 9, and $\lambda_m$ = 605 nm for 10). Unfortunately, no other calculated electron transition energies could be assigned to the broad and weak absorption band at 700–900 nm, even after analyzing the singlet and triplet states of complex 10.

Compared to complexes 8 and 9, complex 10 bears a larger 2,2′:5′,2″-terthiophen-5-yl group. Since such a larger coplanar group presents easy π–π stacking interactions leading to J-aggregates, the red-shift absorption of complex 10 could arise from said J-aggregates. To confirm this hypothesis, we studied the spectral behavior of complex 10 at different concentrations, since aggregation processes are highly dependent on the concentration. As shown in Fig. 5, the increasing concentration of 10 resulted in increasing molar extinction coefficients at 823 nm, suggesting that the broad NIR absorption band of complex 10 is resulted from J-aggregates driven by π–π stacking of the 2,2′:5′,2″-terthiophen-5-yl side chain. It is noted that previously reported photothermal materials were nanoparticles caused by surface plasmon resonance and compounds due to their highly conjugated structures. There were only a few photothermal materials resulting from J-aggregates. To the best of our knowledge, this is the first example of a Möbius aromatic complex with photothermal properties induced by J-aggregates, despite such J-aggregate phenomena being quite common.

The broad and weak absorption at 700–900 nm (Fig. 3) of complex 10 suggests that the aggregation behavior is weak. The spherical shape (see the crystal structure in Fig. 2) of the metal center in complex 10 may account for this weak aggregation: steric effects compete with the π–π stacking of the 2,2′:5′,2″-terthiophen-5-yl groups, leading to weak aggregation. For complexes 8 and 9, the smaller thiophen-2-yl and 2,2′-bithiophen-5-yl side chains do not provide sufficient driving force (π–π stacking) to exhibit such aggregation behavior. Thus, complexes 8 and 9 do not present an absorption band at 700–900 nm induced by J-aggregates.

**Synthesis of osmapentalenofuran 12 with a methacrylate group**

The successful preparation of the photothermal complex 10 inspired us to further develop it into a photothermal material. For this purpose, we introduced an olefinic group on the metalla-aromatic complex, since compounds with olefinic groups can be easily grown into macromolecules by radical polymerization. The incorporation of 10 in a polymer may...
have two effects: first, it can improve the water-solubility and biocompatibility of complex 10; secondly, it may improve to some extent the aggregation behavior of complex 10.

Osmapentalynes with vinyl groups have been successfully prepared in our group.79 Following this direction, treatment of olefinic osmapentalyne 11 with 5-ethylval-2,2′:5′,2′′-terthiophene and water at RT gave methacrylate osmapentalenofuran 12. Complex 12 was characterized by NMR spectroscopy, HRMS, and EA. The $^{31}$P($^1$H) NMR spectrum of complex 12 shows two signals at 10.77 (CPh$_3$) and −17.45 (OsPh$_3$) ppm, while the $^1$H NMR spectrum shows the characteristic OsCH signal at 13.75 ppm. These results confirmed that the metalla-cyclic substructure of complex 12 is similar to that of complex 10. In addition, the methacrylate group in complex 12 was confirmed by two signals observed at 10.99 ppm and $−18.09$ ppm in the $^{31}$P($^1$H) NMR spectrum (Fig. S18†). The absolute molecular weight of metallopolymer 13 was calculated to be 1/21.4 based on the absorption value of 13 (0.3 mg mL$^{-1}$) at 605 nm (Fig. S23†). Both results are close to the polymerization feed ratio (1 : 20).

The molecular weight ($M_w$) and polydispersity index (PDI) of metallopolymer 13 were determined by size exclusion chromatography (SEC) in tetrahydrofuran (THF) to be 1.9 × 10$^4$ g mol$^{-1}$ and 1.20 (Fig. S19†), respectively. It is noted that the metallopolymer may feature a very different hydrodynamic radius versus the narrow polystyrene standards. For comparison, the $M_w$ and PDI of monomer 12 were also examined by the same SEC experiment to be 2.5 × 10$^3$ g mol$^{-1}$ and 1.00 (Fig. S25†), respectively.

To further estimate the molecular weight of metallopolymer 13, we have tried to determine it by inverse gated $^{13}$C($^1$H) NMR spectroscopy. Based on the integral ratio (Fig. S19†) of the terminal ethoxy group (C17 from initiator) versus the methoxy (C9) group in the oligo ethylene glycol side-chains (repeating unit of 14), the absolute molecular weight of metallopolymer 13 was calculated to be about 9500 with the help of the calculated ratio of 12/14 in metallopolymer 13.

As expected, metallopolymer 13 presents good water solubility (3.0 mg mL$^{-1}$ in water), supporting the successful preparation of metallopolymer 13. The most interesting feature of

![Scheme 2](image-url)  
**Scheme 2** Synthesis of osmapentalenofuran 12 with the methacrylate group and metallopolymer 13.
Conclusions

In summary, we have successfully prepared metallapentalenofurans with oligothiophen-5-yl groups under very mild conditions. They are supported by NMR spectroscopy, HRMS, elemental analysis, single-crystal X-ray diffraction, and UV-vis-NIR absorption spectroscopy, as well as by time-dependent DFT calculations. The Möbius aromatic metallapentalenofuran (10) bearing a terthiophene group showed a good photothermal effect induced by the J-aggregates. The temperature of its solution containing 1.00 mg mL\(^{-1}\) of complex 10 in water–ethanol (1/9, v/v) would rise quickly from 28 to 57 °C within 5 min under an NIR irradiation (808 nm, 1.0 W cm\(^{-2}\)). Based on this observation, we prepared another photothermal metallapentalenofuran (12) containing a methacrylate group as a monomer. The monomer was also characterized by different NMR spectroscopy techniques and SEC measurements. The obtained metallopolymer showed both a thermal response and a NIR-light response. This new NIR-responsive metal-containing copolymer represents a new stimuli-responsive metallopolymer.

Fig. 6 (a) Temperature curves of water (solvent) and a solution of metallopolymer 13 (3.0 mg mL\(^{-1}\) in water) irradiated with an 808 nm laser at a power density of 1.0 W cm\(^{-2}\). (b) Solutions of metallopolymer 13 in water before (left) and after (right) NIR irradiation. (c) Temperature curves of a solution of metallopolymer 13 (3.0 mg mL\(^{-1}\) in water) irradiated with an 808 nm laser at a power density of 1.0 W cm\(^{-2}\) with five laser on–off cycles.

Experimental

General information

All syntheses were carried out under an inert atmosphere using standard Schlenk techniques unless otherwise stated. The starting material complex 5,\(^1\) 5-ethynyl-2,2′-bithiophene,\(^{80}\) 5-ethyl-2,2′,5′,2′-terthiophene,\(^{80}\) and complex 11 \(^{70}\) were synthesized according to the previously published literature. The other reagents and solvents were used as purchased from commercial sources without further purification. Column chromatography was performed on alumina gel (200–300 mesh) in air. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AV-400 spectrometer (400 MHz), or a Bruker AV-500 spectrometer (500 MHz) at room temperature. \(^1\)H and \(^{13}\)C\(^{[1]}\)H NMR chemical shifts (\(\delta\)) are relative to tetramethylsilane, and \(^{31}\)P\(^{[1]}\)H NMR chemical shifts are relative to 85% H\(_3\)PO\(_4\). The absolute values of the coupling constants are given in hertz (Hz). Multiplicities are abbreviated as s (singlet), d (doublet), t (triplet), m (multiplet) and br (broad). Elemental analysis (EA) data were collected on a Vario EL III elemental analyzer. The high-resolution mass spectral (HRMS) experiments were performed on a Bruker En Apex Ultra 7.0 T FT-MS. Absorption spectra were recorded on a Shimadzu UV2550 UV-Vis spectrophotometer. The relative molecular weights and molecular weight distribution were determined by size exclusion chromatography (SEC). The SEC system (Agilent 1100 Series) was equipped with a refractive-index detector and gel columns (PSS SDV 100 Å 3 μm and linear S 5 μm) maintained at 35 °C. Tetrahydrofuran was used as the eluent at a flow rate of 1.0 mL min\(^{-1}\). The gel columns were calibrated with narrow-molecular-weight polystyrene standards (PDI \(\leq\) 1.05, Shoko, Japan). The STL808T1-15W fiber-coupled laser system (Stone Company) was used in photothermal experiments and the temperature data were collected by using an FLIR A35 FOV 24 thermal imaging camera.
Complex 8. 2-Ethynylthiophene (80.2 μL, 0.80 mmol) was added to a solution of complex 5 (200 mg, 0.16 mmol) in 10 mL dichloromethane and 0.2 mL water in air. The mixture was stirred at room temperature (RT) for 1 d to afford a red solution. The solution was evaporated under vacuum to a volume of ca. 2 mL, and then was loaded on a neutral alumina column and eluted by the mixture of dichloromethane and acetone (5/1, v/v). The red band was collected, and the solvent was evaporated to dryness under vacuum to afford a red solid. Yield, 120 mg, 55%. 1H NMR plus 1H-13C HSQC (500.2 MHz, CDCl3): δ 13.72 (d, JCPH = 15.3 Hz, 1H, H1), 8.00 (s, 1H, H8), 7.64 (s, 1H, H3, confirmed by 1H-13C HSQC). 13C NMR plus DEPT-135, 1H-13C HSQC and 1H-13C HMBC (125.8 MHz, CDCl3): δ 224.4 (t, JCP = 6.2 Hz, C7), 208.5 (br, C1), 188.5 (s, C9), 181.1 (dt, JCP = 22.0 Hz, JPC = 4.5 Hz, C4), 168.0 (s, C5), 163.2 (s, COOCH3), 144.1 (d, JPC = 19.0 Hz, C3), 140.0 (s, C6), 120.6 (s, C8), 119.3 (d, JCP = 88.4 Hz, C2), 50.8 (s, COOCH3), 140.5-124.9 ppm (other aromatic carbons). Elemental analysis calcd (%) for C69H55ClO3OsP3S: C 60.29, H 3.88; found: C 60.07, H 3.73. HRMS (ESI): m/z calced for [C69H55ClO3OsP3S]+, 1447.2128; found, 1447.2122.

Complex 12. A solution of 5-ethyl-2,2’-3,3’-terthiophene (218 mg, 0.80 mmol) and complex 11 (200 mg, 0.15 mmol) in 10 mL dichloromethane and 0.2 mL water in air was stirred at RT for 1 d to afford a red solution. The solution was evaporated under vacuum to a volume of ca. 2 mL, and then was loaded on a neutral alumina column and eluted by the mixture of dichloromethane and acetone (3/1, v/v). The green band was collected, and the solvent was evaporated to dryness under vacuum to afford a green solid. Yield: 107 mg, 44%. 1H NMR plus 1H-13C HSQC (500.2 MHz, CDCl3): δ 13.72 (d, JCPH = 15.1 Hz, 1H, H1), 7.95 (s, 1H, H8), 7.65 (s, 1H, H3, confirmed by 1H-13C HSQC), 7.59 (s, 1H, H5), confirmed by 1H-13C HSQC), 6.23 (s, 1H, H15), 5.71 (s, 1H, H15), 4.36 (t, JCPH = 4.7 Hz, 2H, H12), 4.23 (t, JCPH = 4.7 Hz, 2H, H11), 2.02 (s, 3H, H16), 7.90-7.00 ppm (52H, other aromatic protons). 31P NMR (202.5 MHz, CDCl3): δ 10.77 (s, CPPh3), −17.45 ppm (s, O3CPPh3). 13C NMR plus DEPT-135, 1H-13C HSQC and 1H-13C HMBC (100.6 MHz, CDCl3): δ 222.4 (t, JCP = 5.9 Hz, C7), 208.6 (br, C1), 187.5 (s, C9), 181.1 (dt, JCP = 22.2 Hz, JPC = 4.1 Hz, C4), 168.3 (s, C5), 163.4 (s, COOCH3), 145.5-124.2 ppm (other aromatic carbons). Elemental analysis calcd (%) for C82H65ClO5OsP3S3: C 88.4 Hz, 1H, H1), 7.95 (s, 1H, H8), 7.65 (s, 1H, H3, confirmed by 1H-13C HSQC), 7.61 (s, 1H, H5, confirmed by 1H-13C HSQC), 7.61 (s, 1H, H5, confirmed by 1H-13C HSQC), 7.59 (s, 1H, H5, confirmed by 1H-13C HSQC), 6.23 (s, 1H, H15), 5.71 (s, 1H, H15), 4.36 (t, JCPH = 4.7 Hz, 2H, H12), 4.23 (t, JCPH = 4.7 Hz, 2H, H11), 2.02 (s, 3H, H16), 7.90-7.00 ppm (52H, other aromatic protons). 31P NMR (202.5 MHz, CDCl3): δ 10.77 (s, CPPh3), −17.45 ppm (s, O3CPPh3). 13C NMR plus DEPT-135, 1H-13C HSQC and 1H-13C HMBC (125.8 MHz, CDCl3): δ 223.7 (br, C7), 209.0 (br, C1), 187.6 (s, C9), 181.1 (dt, JCP = 21.5 Hz, C4), 168.1 (s, C5), 167.2 (s, C13), 162.5 (s, C10), 144.9 (d, JPC = 20.4 Hz, C3), 139.5 (s, C6), 136.0 (s, C14), 126.5 (s, C15), 120.6 (s, C8), 119.3 (d, JCP = 89.2 Hz, C2), 62.8 (s, C12), 61.9 (s, C11), 18.5 (s, C16), 145.4-124.1 ppm (other aromatic carbons). Elemental analysis, calcd (%) for C82H65ClO5OsP3S3: C 60.39, H 3.96; found: C 60.07, H 3.73. HRMS (ESI): m/z calced for [C82H65ClO5OsP3S3]+, 1545.2505; found, 1545.2519.

Metallopolymer 13. An anapole charged with ethyl-2-bromo-isobutanoate (EBIB, 6.6 μL, 0.044 mmol), tris(2-dimethylamino)ethylamine (Me2TREN, 3.2 μL, 0.012 mmol), complex 12 (341.5 mg, 0.22 mmol), triethylglycol methyl ether methacrylate (1.0 mL, 4.42 mmol), and N,N-dimethylformamide (DMF, 5 mL) was deaerated by three freeze–pump–thaw cycles in liquid N2 and then sealed. A copper wire (L = 2 cm) was added to the mixture under a nitrogen atmosphere. The reaction mixture was stirred at RT for 24 h; then, 50 mL diethyl ether–hexane (1:5) was slowly poured into the mixture to afford a green precipitate, which was collected by filtration. The crude product was further purified by redissolving in dichloromethane (3 mL) and poured into diethyl ether (50 mL)
to afford a green solid. An analytically pure sample was thus obtained by repeating this procedure several times. Finally, the product was dried under vacuum to afford metallopolymer 13 as a green solid. Yield: 845.1 mg, 63%. 1H NMR (500.2 MHz, CD2Cl2): δ 13.62 (br, H15), 7.95–6.96 (aromatic protons in osmapentalenofuran units), 4.01 (br, 2H, H3, H12, and H13), 3.59–3.44 (10H, H4–H8), 3.27 (br, 3H, H9), 1.83–1.75 (2H, H2 and H11), 0.96–0.81 ppm (3H, H1 and H10). 31P NMR (202.5 MHz, CD2Cl2): δ 10.99 ppm (s, CPPh3), −18.09 (s, OsPh3). SEC, Mw: 19 018 g mol⁻¹; Mw/Mn: 1.20.

X-ray crystallographic analysis. Single crystals suitable for X-ray diffraction were grown from a dichloromethane solution layered with hexane. Single-crystal X-ray diffraction data for 9 and 10 were collected on a Rigaku R-AXIS SPIDER IP CCD area detector with Mo Kα radiation (λ = 0.71073 Å). Non-absorption corrections were applied to 9 and 10. Using Olex2, the structures of 9 and 10 were solved with the XS2 structure solution program using the Patterson method and refined with the ShelXL refinement package using least squares minimization. All non-hydrogen atoms were refined anisotropically unless otherwise stated. Hydrogen atoms were placed at idealized positions by assuming the riding model. Some of the solvent molecules and phenyl groups were disordered and refined with suitable restraints. CCDC 1814896 (9) and 1814898 (10) contain the supplementary crystallographic data for this paper.

Crystal data for complex 9. C22H44BCl2F2O2OsP2 (C22H57ClO3OsP2S2)BrF42CH2Cl2 (Mf = 1621.52 g mol⁻¹): monoclinic, crystal dimension 0.10 × 0.10 × 0.10 mm, space group P21/c (no. 14), a = 24.7978(6) Å, b = 14.1129(3) Å, c = 20.1547(4) Å, β = 96.6450(10)°, V = 7006.1(3) Å³, Z = 4, T = 173 K, μ(MoKα) = 2.198 mm⁻¹, Dc calc. = 1.537 g mm⁻³, 102 445 reflections measured (6.006 ≤ Θ ≤ 54.966), 16 024 unique (Rint = 0.1045, Rsigma = 0.0676), were used in all calculations. The final R1 was 0.0503 (I > 2σ(I)) and wR2 was 0.1469 (all data), GOF = 1.110. Residual electron density (e Å⁻³) max/min: 2.38/–2.72.

Crystal data for complex 10. C22H55BClF2OsP3S (C22H59ClO3OsP3S2)BrF4 (Mf = 1533.79 g mol⁻¹): triclinic, crystal dimension 0.25 × 0.20 × 0.20 mm, space group P1 (no. 2), a = 11.1803(3) Å, b = 14.1709(4) Å, c = 23.4379(6) Å, α = 76.6530 (10)°, β = 84.0290(10)°, γ = 69.3370(10)°, V = 3379.62(16) Å³, Z = 2, T = 173 K, μ(MoKα) = 2.150 mm⁻¹, Dc calc. = 1.507 g mm⁻³, 54 869 reflections measured (6.016 ≤ Θ ≤ 54.968), 15 481 unique (Rint = 0.0842, Rsigma = 0.0775), which were used in all calculations. The final R1 was 0.0626 (I > 2σ(I)) and wR2 was 0.1752 (all data), GOF = 1.031. Residual electron density (e Å⁻³) max/min: 1.57/–2.82.

Computational details. All the calculations were performed with the Gaussian 09 software package. The B3LYP/6-31G** level of density functional theory was used to optimize all the structures studied in this work. In the B3LYP calculations, the effective core potentials (ECPs) of Hay and Wadt with a double-ζ valence basis set (LanL2DZ) were used to describe Os, S, and P atoms, whereas the standard 6-31G** basis set was used for C, O, and H atoms. Polarization functions were added for Os (ζ(f) = 0.886), S (ζ(d) = 0.421), and P (ζ(d) = 0.340). We calculated the UV-Vis absorption spectra of the cationic part of 8, 9, and 10 using the PCM model with dichloromethane as the solvent.

Conflicts of interest
There are no conflicts to declare.

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References


