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ARTICLE TYPE

Colorless metallodithiolene oligomers and polymers with intense near- and mid-infrared absorption

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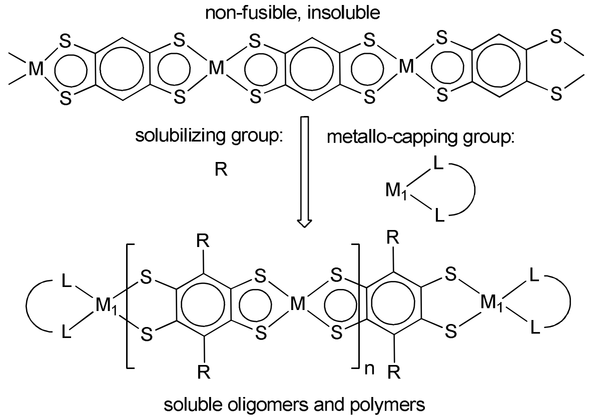
Reported herein are the syntheses and properties of a series of multi-nuclear metallodithiolene complex oligomers (**5**, **6** and **7**) and homologous polymer (**8**). The Ni/Pd-dithiolene complexes **5**, **6** and **7** are characterized by intense absorption in the spectral region of 1000 – 1800 nm with a high molar absorption coefficient (e.g., 10^5 $M^{-1}cm^{-1}$ at 1257 nm for **7**). Complex polymer **8** is readily soluble in common organic solvents and shows remarkably broad and intense absorption in the entire near- and mid-infrared spectral region (800 nm – 25 μm). The films of these metallodithiolene materials exhibit good visual transparency or extremely weak absorption in the visible region, making them potentially useful as excellent colourless infrared absorbers.

1 Introduction

Metallodithiolene complexes have been subjected to fundamental studies since 1960s,[1-5] and are characterized by the planar five-membered metallocycle fused with aromatic rings and extended π-electron delocalization along the entire molecular skeleton.[6-8] This class of metal complexes exhibit unique electrical,[9,10] nonlinear optical,[8,11,12] and magnetic properties[13] with potential applications in optoelectronics.[14-16] Heeger and co-workers investigated conductivity and magnetism of metal poly(benzodithio1ene)s in 1980.[2] Similar metal complex polymers such as poly(tetrathiosquarates), poly(ethylenetetrathiolates), poly(tetrathiafulvalenetetrathiolates), and poly(tetrathiooalates) were also reported[1,3,17-19] and some of them showed high conductivity[17-19] and magnetism.[2] However, in-depth study and applications of metallodithiolene polymers are seriously hindered by poor solubility and incomplete characterizations.[2,17-19] The low-energy light-absorbing materials, especially those that are colorless or visually transparent and highly absorbing in the infrared (IR) or specifically in near-infrared (NIR, e.g., 800–2500 nm) and mid-infrared (MIR, e.g., 2.5–25 μm) regions, are scarce but fundamentally interesting and practically useful for applications in photonics and energy-saving thermal conversions.[20] The Müllen group reported many rylenediimide dyes that show a maximal absorption (λ_{max}) up to 953 nm with a weak absorption at the visible spectral region.[21-23] Another colorless, selective NIR-absorbing dye is based on the boron-coordinated diketopyrrolopyrrole system and has λ_{max} at 941 nm.[24-26]

Metallodithiolene complexes are usually colored and can also be NIR-absorbing, typically from 700 to 1600 nm, depending on the nature of substituent groups on the metallocyclic unit.[27-31] Similarly, metallodithiolene polymers should also be NIR-absorbing, due to the presence of the low-energy mixed-valence.[2] However, except for structurally ill-defined halogen-substituted nickel benzodithiolene oligomers having a maximal absorption around 1800 nm,[32] there is no report to date on structurally well-defined, colorless and low-energy light-absorbing metallodithiolene polymers. Further research is needed to address a fundamental question of how far into the red spectral region metallodithiolene polymers can absorb and to search for new colorless IR absorbers for photonics applications.

Structurally well-defined soluble metallodithiolene oligomers and polymers were designed by molecular manipulation at the lateral positions and chain ends of non-fusible and insoluble metal poly(benzodithiolene)s (Scheme 1). A fused metallodithiolene backbone or ribbon-like skeleton with the extended conjugation is expected to lead to some unique optical and other properties.[1,2,17-19,33] The pendant groups are typically long alkyl chains and can impart a good solubility to the target polymers. In order to avoid the oxidization of the thiol groups at



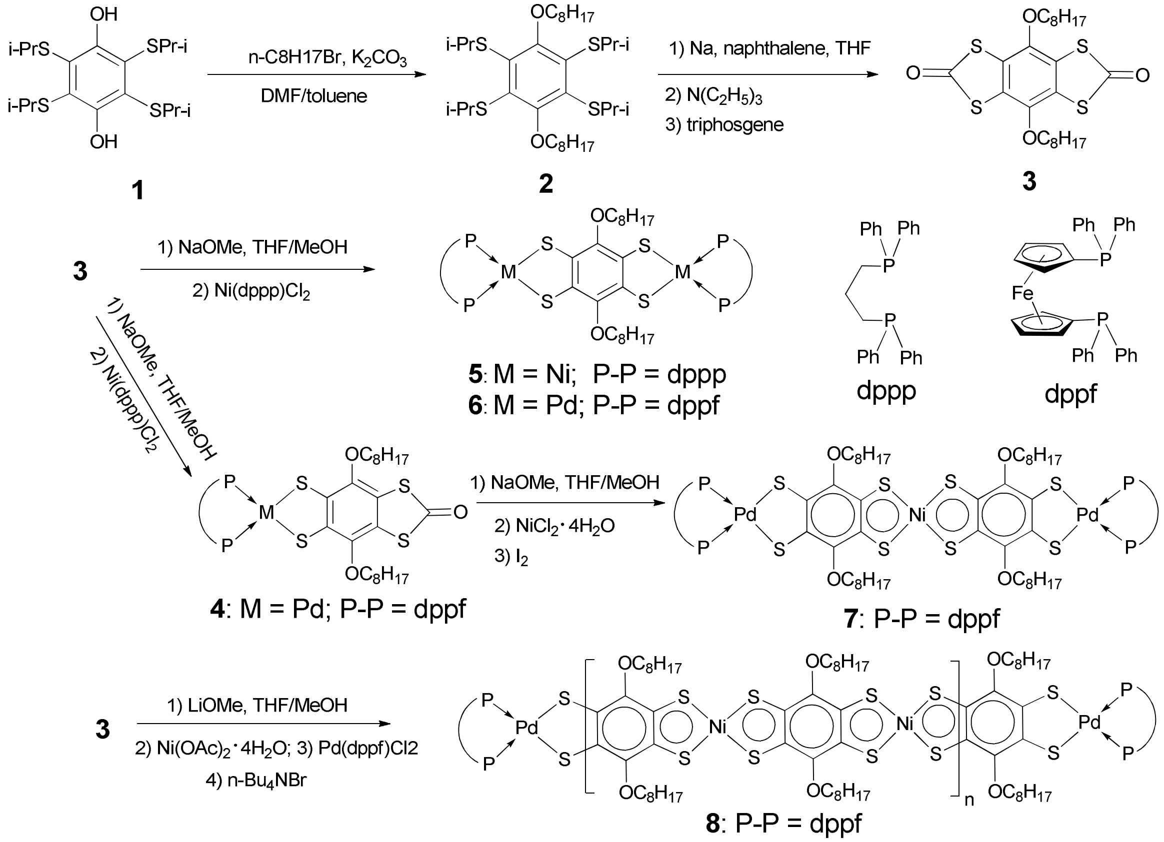
Scheme 1 Conceptual design of well-defined soluble metallodithiolene oligomers and polymers by introduction of the solubilizing pendant and metallo-end capping groups.

the polymer chain ends, a metallo-capping group of M^1L_2 will be used. The end-capping also allows for characterizations of molecular weight and chemical structures by determination of the ratios of two different metals (M/M^1) in the mainchain and at the chain ends. Through controlled stepwise syntheses, a series of soluble metallobenzodithio1ene oligomers **5-7** (λ: 1000 – 1800 nm) and polymer **8** (λ: 800 nm – 25 μm) with well-defined structures can be made available for in-depth study on the optical properties.

2 Experimental

2.1 Materials

All the reagents were used as received from Alfa Aesar, Acros Organics and Aldrich Chemicals. Air- and moisture-sensitive syntheses were carried with the standard Schlenk techniques in a Schlenk tube under argon atmosphere. Compounds **1-3** were synthesized according to the procedures reported in literature.[34-36] The synthesis and characterizations for **1-3** are given in Support Information.



Scheme 2 Synthetic route to metallodithiolene oligomers **4-7** and polymer **8**.

2.2 Methods

NMR spectra were recorded on Bruker Avance 300 (300 MHz) and Bruker Avance 400 (400 MHz) NMR spectrometers. Chemical shifts (ppm) are given relative to CDCl3, 7.26 ppm (^1H NMR) and 77.16 ppm (^{13}C NMR), with TMS as internal reference and H_3PO_4 as external reference for ^{31}P NMR spectra, respectively. All the measurements were carried out at room temperature unless otherwise stated. All the compounds were characterized by MS (mass spectroscopy): MALDI-TOF-MS were obtained from Bruker Daltonics Autoflex III time-of-flight (TOF) mass spectrometry; Electron impact mass spectrometry (EI-MS) were recorded on Agilent Technologies 5975 mass spectrometer and Elaectrospray ionization mass spectrometry (ESI-MS) were recorded on Waters Quattro Premier XE. Elemental analysis was performed on Elementar Vario EL cube analyzer. Thermogravimetric analysis (TGA) was performed on a PerkinElmer Pyris Diamond TG from 50 to 800 ºC at a heating rate of 10 ºC /min under a continuous nitrogen flow. The analysis of metals (Ni and Pd) was carried on inductive coupled plasma optical emission spectrometer (Thermo Scientific iCAP 6000). Molecular weight of the polymer was determined on a Waters 1515 Gel Permeation Chromatography (GPC). UV-VIS-NIR spectra (3300–300 nm) were recorded using a Shimadu UV-3600 Spectrophotometers. IR spectra (4400–400 cm^{-1}) were recorded using a Shimadu FT-IR Affinity-1 Spectrometer. Cyclic voltammetry (CV) was performed on a CHI660B electrochemical workstation, using a conventional three-electrode cell consisting of a platinum disk or glass-carbon as the working electrode, a platinum wire as the counter-electrode and Ag/Ag^+ in a 0.01 $mol\cdot dm^{-3}$ of $AgNO_3$ solution as the reference electrode. The experiments were performed at room temperature (25 °C) in dry DCM or CH_3CN containing 0.1 $mol\cdot dm^{-3}$ Bu_4NPF_6 as the supporting electrolyte, at a scan rate of 100 $mV\cdot s^{-1}$.

2.3 Synthesis

As shown in Scheme 2, detailed syntheses of complexes **4-8** are given below. Detailed syntheses of **1-3**, NMR and MS spectra are provided in the ESI.†

Complex 4. A 50-mL Schlenk flask equipped with a stirring bar was charged with **3** (154.4 mg, 0.30 mmol), NaOMe (40.7 mg, 0.75 mmol) and 30 mL of THF/MeOH (1:1 v/v). The resulting bright yellow solution was stirred at ambient temperature under argon for 2.5 hours, followed by addition of Pd(dppf)Cl_2 (219.5 mg, 0.30 mmol). After 15 hours, the solvent was removed and the yellow residue was purified on a silica gel column eluted with CH_2Cl_2/petroleum ether (3:1 v/v) to give orange solids (308.8 mg, 89.7% yield). ^{1}H NMR (δ, ppm in $CDCl_3$) 7.71-7.80 (q, 8H, J = 4.4, 7.2 *Hz*, aromatic CH), 7.42-7.49 (t, 4H, J = 7.2 *Hz*, aromatic CH), 7.31-7.38 (t, 8H, J = 7.2 *Hz*, aromatic CH), 4.42 (s, 4H, Fc-H), 4.28 (s, 4H, Fc-H), 3.72-3.77 (t, 4H, J = 6.8 *Hz*, -OCH_2), 1.42-1.49 (m, 4H, O-CH_2-CH_2), 1.33-1.18 (overlapping br, m, 20H, aliphatic CH_2), 0.82-0.92 (t, 6H, J = 6.8 *Hz*, CH_3); ^{31}P NMR (δ, ppm in $CDCl_3$) 24.67; ^{13}C NMR (δ, ppm in $CDCl_3$) 193.18, 145.58, 141.91, 134.89, 132.44, 131.97, 130.88, 127.92, 119.19, 76.16, 75.14, 74.59, 73.17, 71.73, 31.87, 30.09, 29.45, 29.31, 25.87, 22.68, 14.12; MS (MALDI-TOF): 1147.4 (M^+); Anal. Calcd for $C_{57}H_{62}FeO_3P_2S_4$: C, 59.66; H, 5.45; Fe, 4.87; P, 5.40; Pd, 9.27; S, 11.18; Found: C, 59.68; H, 5.47; Fe, 4.95; P, 5.46; Pd, 9.28; S, 11.21.

Complex 5. A 50-mL Schlenk flask equipped with a stirring bar was charged with **3** (257.4 mg, 0.50 mmol), NaOMe (124.2 mg, 2.30 mmol) and 30 mL of THF/MeOH (1:1 v/v). The resulting bright yellow solution was stirred at ambient temperature under argon for 3 hours, followed by addition of Ni(dppp)Cl_2 (547.5 mg, 1.01 mmol). After 15 hours at ambient temperature, the reaction mixture was filtered and dark green precipitate was purified on a silica gel column eluted with CH_2Cl_2/EtOAc (10:1 v/v) to give dark green powders (527.8 mg, 75.3% yield). ^{1}H NMR (δ, ppm in $C_6D_4Cl_2$, 40 °C) 7.55-7.64 (br, 16H, aromatic CH), 7.30-7.33 (t, 8H, J = 7.2 *Hz*, aromatic CH), 7.21-7.30 (t, 16H, J = 6.8 *Hz*, aromatic CH), 3.38-3.43 (t, J = 7.6 *Hz*, -OCH_2), 2.40-2.65 (br, 8H, Ph-$(CH_2)_3$-Ph), 2.03-2.25 (br, 4H, Ph-$(CH_2)_3$-Ph), 1.15-1.34 (overlapping br, 16H，aliphatic CH_2), 1.04-1.13 (m, 4H, aliphatic CH_2), 0.94-1.01 (m, 4H, aliphatic CH_2), 0.89-0.92 (t, 6H, J = 6.4 *Hz*, CH_3); ^{31}P NMR (δ, ppm in $C_6D_4Cl_2$, 40 °C) 12.00; ^{13}C NMR (δ, ppm in $C_2D_2Cl_4$, 40 °C) 133.86, 133.37, 130.90, 130.15, 127.96, 126.07, 70.89, 32.10, 30.16, 29.58, 29.44, 26.02, 22.88, 19.45, 14.39; MS (MALDI-TOF): 1398.3 (M^+); Anal. Calcd for $C_{24}H_{34}O_4S_4$: C, 65.15; H, 6.19; P, 8.84; S, 9.15; Ni, 8.38; Found: C, 65.16; H, 6.16; P, 8.90; S, 9.21; Ni, 8.31.

Complex 6. As for the preparation of **5**, compound **3** (103.0 mg, 0.20 mmol) and Pd(dppf)Cl_2 (292.7 mg, 0.40 mmol) were used. After purification by chromatography(CH_2Cl_2/EtOAc, 5:1 v/v), complex **6** was obtained as brown powders (303.4 mg, 85.2% yield). ^{1}H NMR (δ, ppm in $CDCl_3$) 7.87 (s, br, 16H, aromatic CH), 7.47-7.4 (m, br, 24H, aromatic CH), 4.44 (s, 8H, Fc-H), 4.37(s, 8H, Fc-H), 3.58 (t, br, 4H, -OCH_2), 1.21-1.33 (overlapping br, m, 20H, aliphatic CH_2), 1.12 (m, br, 4H, aliphatic CH_2), 1.00 (t, br, 6H, CH_3); ^{31}P NMR (δ, ppm in $C_2D_2Cl_4$) 24.81; ^{13}C NMR (δ, ppm in $C_2D_2Cl_4$, 40 °C) 135.04, 130.54, 128.04, 124.88, 119.31, 111.44, 109.54, 72.85, 72.50, 69.55, 59.51, 32.00, 30.34, 29.64, 29.37, 26.21, 22.89, 14.25; MS (MALDI-TOF): 1778.1 (M^+).

Complex 7. A 50-mL Schlenk flask equipped with a stirring bar was charged with complex **4** (113.6 mg, 0.099 mmol), NaOMe, (27.0 mg, 0.50 mmol) and 30 mL of DCM/MeOH (1:1 v/v). The resulting orange solution was stirred at ambient temperature under argon for 3 hours, followed by addition of $NiCl_2\cdot 6H_2O$ (11.9 mg, 0.05 mmol). After stirring for 23 hours at ambient temperature, I_2 (27.9 mg, 0.11 mmol) was added. After 1 hour, the reaction mixture was filtered and the red solid was purified on a silica gel column eluted with CH_2Cl_2/EtOAc (30:1 v/v) to give **7** as dark brownish red solids (67.7 mg, 59.5% yield). ^{1}H NMR (δ, ppm in $CDCl_3$) 7.69 (br s, 16H, aromatic CH), 7.31-7.40 (overlapping br, s, 8H, aromatic CH), 7.14-7.36 (overlapping br, s, 16H, aromatic CH), 4.35 (s, 8H, Fc-H), 4.21 (s, 8H, Fc-H), 3.86 (br, s, 8H, -OCH_2), 1.61 (br, s, 8H, O-CH_2-CH_2), 1.23 (br, s, 40H, aliphatic CH_2), 0.83 (br, s, 12H, CH_3); ^{31}P NMR (δ, ppm in $CDCl_3$) 25.57; MS (MALDI-TOF): 2294.2 (M^+); Anal. Calcd for $C_{112}H_{124}Fe_2NiO_4P_4Pd_2S_8$: C, 58.54; H, 5.44; Fe, 4.86; Ni, 2.55; P, 5.39; Pd, 9.26; S, 11.16; Found: C, 58.48; H, 5.36; Fe, 4.95; Ni, 2.48; P, 5.36; Pd, 9.21; S, 11.13.

Polymer 8. A 25-mL Schlenk tube equipped with a stirring bar was charged with **3** (257.4 mg, 0.50 mmol), LiOMe (87.5 mg, 2.30 mmol) and 10 mL of THF/MeOH (7:3 v/v). The resulting bright yellow solution was stirred at 40 °C under argon for 3 hours, followed by addition of $Ni(OAc)_2\cdot 4H_2O$ (124.4 mg, 0.50 mmol). After stirring at 60 °C for 26 hours, Pd(dppf)Cl_2 (36.5 mg, 0.05 mmol) was added and the reaction mixture was kept at 60 °C for another 2 hours. Then, Bu_4NBr (322.4 mg, 1.00 mmol) was added and the resulting dark green suspension was stirred at 60 °C for 2 hours. After cooling to ambient temperature, the suspension was centrifuged and the residue was washed with methanol 3-4 times. The polymer was further washed in a Soxlet extractor with methanol first and then with dichloromethane. Polymer **8** was obtained as black solids (365.5 mg). ^{31}P NMR (δ, ppm, $CDCl_3$) 25.79; Anal. Calcd for polymer **8** Found: C, 60.85; H, 9.96; N, 2.19; S, 13.83; Anal by ICP: Ni, 8.04%; Pd, 0.00721%; GPC: $M_n = 1.0 \times 10^6$, PDI = 1.12.

3 Results and discussion

3.1 Design and synthesis

The synthetic routes to the target complexes **4-8** are shown in Scheme 1b and involve the use of ligand precursor **3** as a key starting material and a latent ligand for complex formation. Compound **3** with the pendant octoxy groups was derived from thioethers **2** in one pot via two steps, which was synthesized by alkylation of the compound **1**.[34] Compound **3** is more stable in air than the benzenetetrathiol ligand,[37] and can be used directly for complex formation by in-situ removal of the carbonate protecting group by sodium or lithium methoxide. Thus, dinuclear Ni and Pd complexes **5** and **6** were obtained in nearly quantitative yields upon treatment of compound **3** with sodium methoxide, followed by reaction or capping with Ni(dppp)Cl_2 or Pd(dppf)Cl_2, respectively.[38,39] The synthesis of Ni/Pd trinuclear complex **7** involved the use of unsymmetric mono-nuclear complex **4** containing one latent dithio-ligand, which was readily prepared in high yield by selective removal of one carbonate group of compound **3** and subsequent reaction with Pd(dppf)Cl_2. The Pd-P and Pd-S bonds in **4** are chemically inert to sodium methoxide during removal of the carbonate group and the in-situ generated dithiol readily reacts with $NiCl_2$ to form the desired trinuclear complex **7**. To facilitate purification by chromatography and characterizations of trinuclear complex **7**, the NiC_4S_4 unit was oxidized by I_2 to the neutral valence state. The high-yield syntheses of complexes **4-7** confirmed the synthetic strategy based on the use of latent ligand **3** and the end-capping reaction. Accordingly, polymer **8** was synthesized from the ligand precursor **3** by treatment with lithium methoxide and then nickel acetate in a mixture of THF and MeOH. Polymer **8** was isolated easily in the ionic form with Bu_4N^+ as a counter ion. Metallodithiolene complexes **4-7** are readily soluble in common solvents, such as acetone, 1,1,2,2-tetrachloroethane, dichloromethane and chloroform. As expected, polymer **8** is also soluble in chloroform (<1.0 mg/mL), dichloromethane (<1.0 mg/mL) and N,N-dimethylformamide (>10 mg/mL).

3.2 Measurement and characterization

Metallodithiolene complexes **4-7** were fully characterized by spectroscopic means and element analysis. The ^1H NMR spectra of **4-7** are well resolved at room temperature or at higher temperatures, although the ^{13}C NMR data are less informative (SI-4). The NMR peaks at 6.98-8.12 and 3.65-3.80 ppm are assigned to the aromatic protons of the phenyls of the phosphine moiety and O-CH_2 of the octoxy chains, respectively. The ^{31}P NMR resonance peaks around 12 and 25 ppm are clearly evident for the presence of the bis(phosphine) moiety in complexes **4-7**, confirming the successful capping reaction. The mass spectroscopy and elemental analysis also confirmed the expected structures of these complexes (SI-3 and SI-4).

The structure and molecular weight of polymer **8** was characterized by $^1H/^{31}P$ NMR, ICP and GPC. The ^{31}P NMR peak at 25.79 ppm confirms the successful end-capping reaction with Pd(dppf) (Fig. S4). However, the ^1H NMR spectrum was poorly resolved and not useful for determining the molecular weight by end-group analysis. The analysis by gel permeation chromatography shows the apparent number-average molecular weight of 1.0 x 10^6 and a narrow polydispersity index of 1.12 (SI-8). Calculation from the content of Ni (8.04%) and Pd (0.00721%) determined by ICP analysis shows the molecular weight of 2.3 x 10^4 or equivalent of 41 repeating units (R_2PhS_4Ni) for polymer **8**. The repeating unit of polymer **8** is not neutral and not fully charged (-2e). The polymer is in the mixed valence state or partially charged with Bu_4N^+ as the counter ion. Therefore, the actual CHNS composition should be between those for the neural state and that of the fully charged state. Indeed, the measured compositions for polymer **8** are 60.85% (C), 9.96 (H), 2.19% (N), and 13.83% (S). The ribbon-like polymer **8** is more rigid than polystyrene, making its molecular weight as determined by GPC is apparently high. The molecular weight as determined by ICP is calculated from the Ni content in the mainchain and the Pd content at the chain ends and is thus deemed more accurate.

Cyclic voltammetry reveals two reversible redox couples for complexes **4-7** (Fig. S5), being consistent with some unsubstituted benzene-1,2,4,5-tetrathiolate analogues.[39] The oxidation potential correlates with the metal nuclear numbers and conjugation length of these metallodithiolene complexes. The band gaps of complexes **5, 6** and **7** were calculated to be 0.72 eV and 0.63 eV (Table 1), respectively.

Table 1 HOMO and LUMO levels and band gaps of complexes 4-7

	$E_{1/2}$(V)	HOMO (eV) [a]	HOMO (eV) [a]	Eg (eV)
4	0.72	-5.45	-3.54[b]	1.91[c]
5	0.33	-5.05	-4.33 [b]	0.72 [c]
6	0.21	-4.94	-4.22 [b]	0.72 [c]
7	0.53	-5.25	-4.72	0.63 [c] /0.53 [a]

[a] Calculated from the formula, $E_{(HOMO)} = -(E_{ox} + 4.80)$ (eV), $E_{(LUMO)} = -(E_{red} + 4.80)$ (eV), [b] Calculated from the formula, $E_{(LUMO)} = E_{g\ opt} + E_{HOMO}$ (eV), [c] Calculated from the formula, $E_{g\ opt} = 1024/\lambda^{abs}_{onset}$ (eV).

3.3 Near- and Mid-Infrared absorption and transparency properties

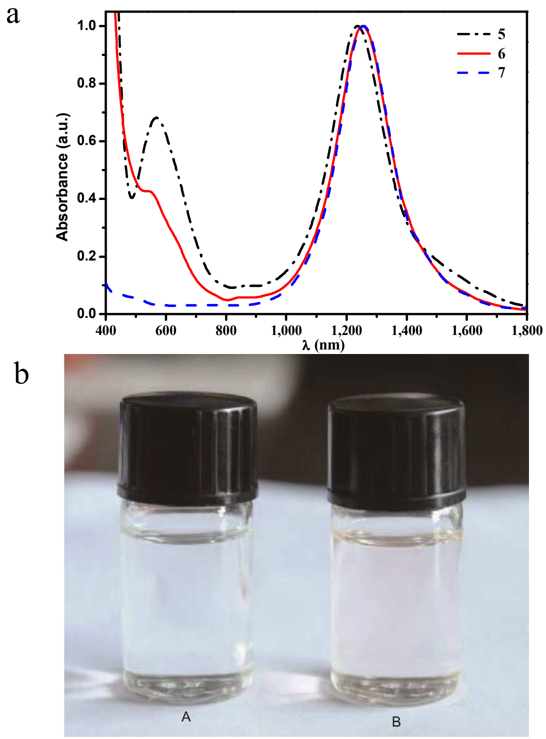


Fig. 1 (a) Absorbance of metallodithiolene complexes **5** (λ_{max}= 1237 nm, ε_{max} =0.9 x 10^4 $M^{-1}cm^{-1}$), **6** (λ_{max} = 1253 nm, ε_{max} =1.2 x 10^4 $M^{-1}cm^{-1}$) and **7** (λ_{max} = 1257 nm, ε_{max} = 1 x 10^5 $M^{-1}cm^{-1}$) in dichloromethane at room temperature. (b) Transparency comparison of photo A) pure dichloromethane and (photo B) **7** in dichloromethane (1.68 x 10^{-5} mol/L), showing visual transparency of **7**.

Mono-nuclear complex **4** absorbs in the UV-vis spectral region with a maximal absorption (λ_{max}) at 430 nm. Complexes **5**, **6** and **7** show long-wavelength absorption from 900 to 1800 nm with λ_{max} between 1237 and 1257 nm, respectively (Fig. 1a). It should be pointed out that trinuclear complex **7** has a high molar absorption coefficient (10^5 $M^{-1}cm^{-1}$) near the telecommunication wavelength of 1300 nm and is visually transparent between 400 nm and 900 nm. In comparison, a solution of **7** in dichloromethane (6 x 10^{-4} mol/L) shows similar visual transparency (photo B, Fig. 1b) as pure dichloromethane (photo A, Fig. 1b). The analogous dinuclear complexes **5** and **6** show similar characteristics in the NIR absorption but lower absorbance (~10^4 $M^{-1}cm^{-1}$) than **7**, indicating that the different metal nuclei (Ni, Pd) does not affect the absorption property.

Therefore, it could be expected that complex **7** (Pd-Ni-Pd) and its Ni-Pd-Ni and Ni-Ni-Ni analogs would have quite similar absorption profile. Going from complex **4** to **5/6** and from **5/6** to **7**, λ_{max} is red shifted 807 nm and 20 nm, respectively. Accordingly, as the number of metal nuclei increases, higher homologous complex oligomers and polymers can be expected to absorb at even longer wavelengths beyond 2000 nm.

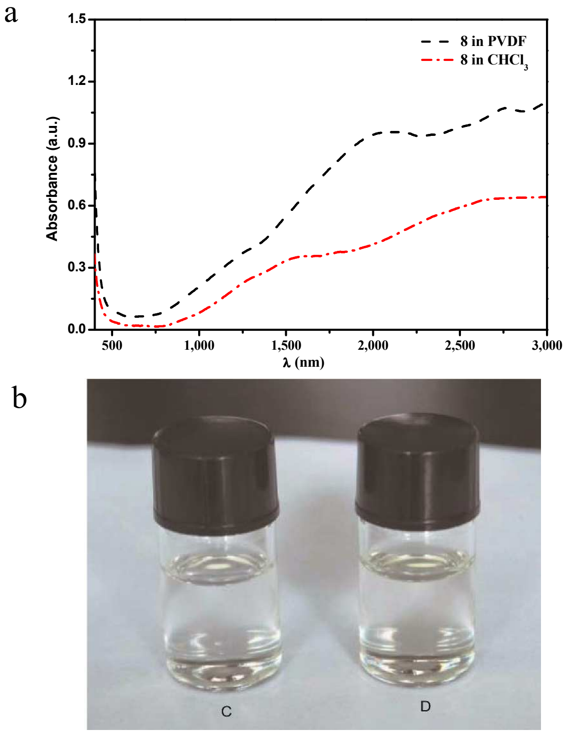


Fig. 2 (a) Absorbance of polymer **8** (225 μg) in PVDF (75 mg) and in chloroform (0.3 mg/mL). (b) Transparency comparison of (photo C) pure chloroform and (photo D) **8** in chloroform (0.3 mg/mL), showing visual transparency of **8**.

Surprisingly, unlike complexes **5, 6** and **7**, polymer **8** in chloroform or doped in poly(vinyl difluoride) (PVDF) absorbs the light so broadly and intensely in the entire NIR spectral region (750–2500 nm) and beyond 3000 nm (Fig. 2a). In comparison, a solution of **8** in chloroform (0.3 mg/mL) (photo D, Fig. 2b) shows similar visual transparency as pure chloroform (photo C, Fig. 2b).

To confirm a complete removal of the cyclic thio-carbonate group during the synthesis, the IR spectra were taken at room temperature using each of the complexes in a given loading weight in KBr pellet (Fig. 3a). Evidently, the band at 1639 cm^{-1}, which is attributed to the carbonyl group of complex **4**, is absent in the spectra of complexes **5**, **7** and **8**. Unlike complexes **4**, **5** and **7**, polymer **8** is characterized by a broad, nearly featureless band between 4000 and 400 cm^{-1} (Fig. 3a). To reveal its absorption in the MIR region, polymer **8** was further measured by IR spectroscopy from 2.5 μm (4000 cm^{-1}) to 25 μm (400 cm^{-1}). As shown in Fig. 3b, polymer **8** absorbs the entire NIR and MIR spectral region from 800 nm and 25 μm with a maximum at 4 μm. Such a remarkably broad and intense absorption is attributed to the extended conjugation and multi-nuclear system in polymer **8**. The CV scan shows multiple oxidation processes (Fig. S7), which implies the presence of continuous multiple band gaps and correlates to the observed broad low-energy absorption. Furthermore, it is visually transparent and virtually has no absorption between 400 and 750 nm, making polymer **8** potentially useful as a unique colorless IR absorber.

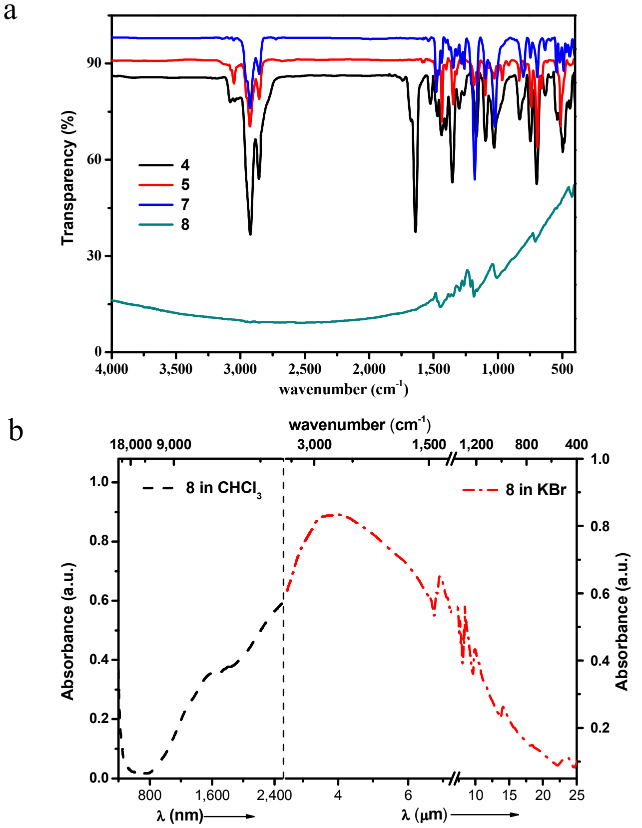


Fig. 3 (a) IR spectra of complexes **4** (0.5 mg), **5** (0.7 mg), **7** (0.8 mg) and polymer **8** (0.2 mg) in KBr (120 mg) pellets taken at room temperature. (b) Absorption of polymer **8** in the vis-NIR (400 – 2500 nm) and MIR (2.5 – 25 μm) regions measured by UV-vis-NIR spectrometry of **8** in $CHCl_3$ (0.3 mg/mL) and IR spectrometry of **8** in a KBr pellet (**8**/KBr = 0.3 mg/120 mg), respectively.

Based on their unique low-energy light-absorbing properties, complex **7** and polymer **8** were further investigated as colorless infrared radiation-absorbing film materials. Details on film preparations and measurements are given in supporting information (SI-9 and SI-10). Complex **7** was then doped in poly[styrene-co-(methyl methacrylate) (PSMMA) and the resulting film showed the identical absorption spectrum (Fig. 4a) as the one in dichloromethane (Fig. 1a) and displays high transmittance in the visible region (Fig. 4e). With increase of the content of complex **7** in the film, the transmittance near the telecommunication wavelength of 1300 nm decreases noticeably and drops to 45% with only 0.8 wt% of complex **7**. The cast films of polymer **8** in PVDF are uniform and able to block most of the NIR light (800–2500 nm) (Fig. 4b**)** and MIR light (2.5 – 6.8 μm), while showing high transmittance visually (Fig. 4f). The films containing complex **7** and polymer **8** are visually colorless and exhibit intense absorption at particular infrared spectral regions (Fig. 4c and 4d). Therefore, complex **7** and polymer **8** could be used as a colorless absorber for attenuating specifically the telecommunication band of 1300 nm and as a colorless filter for blocking off the entire NIR and MIR light, respectively.

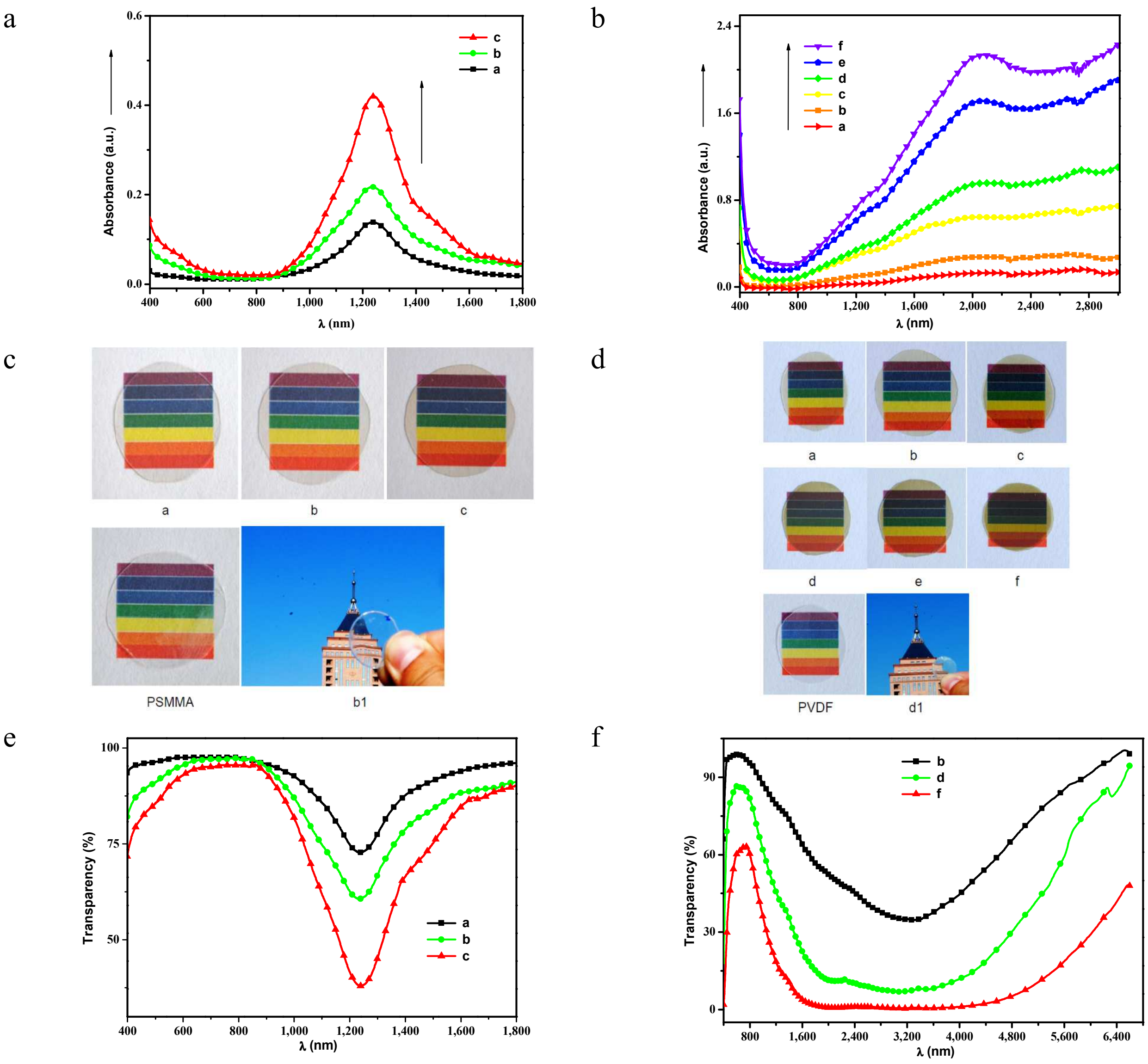


Fig. 4 (a) The absorption spectra of the films with different mass radios of **7**/PSMMA: a (0.3 wt%), b (0.4 wt%), c (0.8 wt%). (b) the absorption spectra of the films of 8 with a different weight blended in PVDF (75 mg): a (0.07 wt%), b (0.1 wt%), c (0.17 wt%), d (0.3 wt%), e (0.5 wt%), f (0.63 wt%). (c) Photos of the films of **7** in PSMMA with different mass radios of **7**/PSMMA (a-c), pure PSMMA and b (0.4 wt%) taken with the building as the background name as b1. The transparency comparison of PSMMA film and films a-c indicates visually colorless NIR absorption. (d) Photos of the films of **8** blended in PVDF with different weights (a-f), pure PVDF and d (0.3 wt%) taken with the building as the background named as d1. The transparency comparison of PVDF film and films of **8** blended in PVDF indicates nearly colorless NIR and mid-IR absorptions. (e) Transmittances of the films of **7** doped in PSMMA with different weights (a-c). (f) Transmittances of the films of the films of **7** doped in PSMMA with different weights (b, d, f).

4 Conclusions

An unusual class of low-energy light absorbing metallodithiolene oligomers and polymers are successfully realized and explored. The multi-nuclear metallodithiolene complexes **5**, **6** and **7** are highly absorbing within a range of the second (1310 nm) and third (1500 nm) telecommunication bands. The complex polymer **8** is solution-processable for thin film applications and shows remarkable broad and intense absorption from 800 nm to 25 μm with λ_{max} at 4 μm. Furthermore, the films of **7** and **8** doped in a host polymer are visually transparent, making them potentially useful as unique colorless IR-selective absorbers for emerging applications in infrared photodetectors, thermovoltaics and other photonic devices.

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† Electronic Supplementary Information (ESI) available: Detailed experimental procedures of compound **1-3**, TGA traces, absorption, MS and NMR spectra, cyclic voltammograms and film preparation. See DOI: 10.1039/b000000x/

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