

**Supporting Online Material**

**Photo-controllable Tristability of a Dithiolato-Bipyridine Pt Complex Molecule  
Containing Two Azobenzene Moieties**

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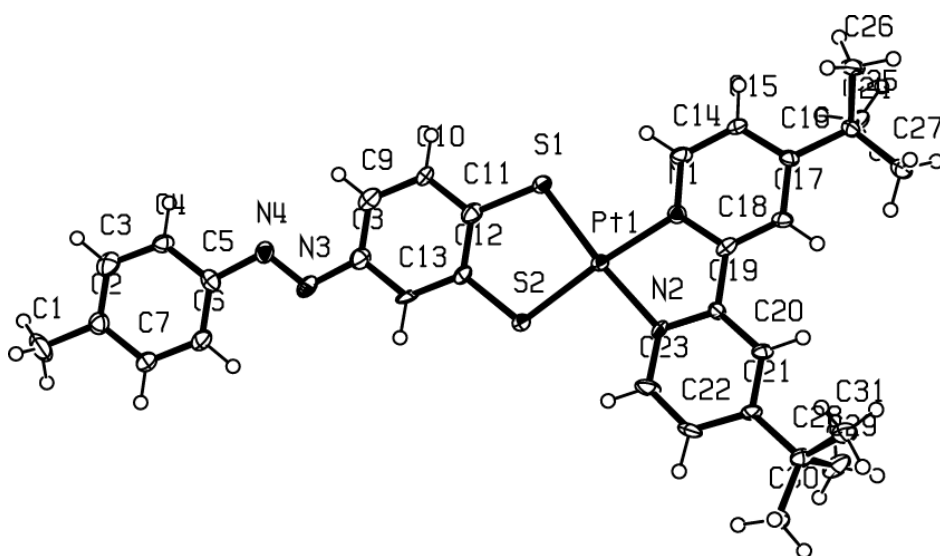


Fig. S1 An ORTEP drawing of complex **1** ( $C_{31}H_{34}N_4PtS_2$ ) with thermal ellipsoid set at the 50% probability level.

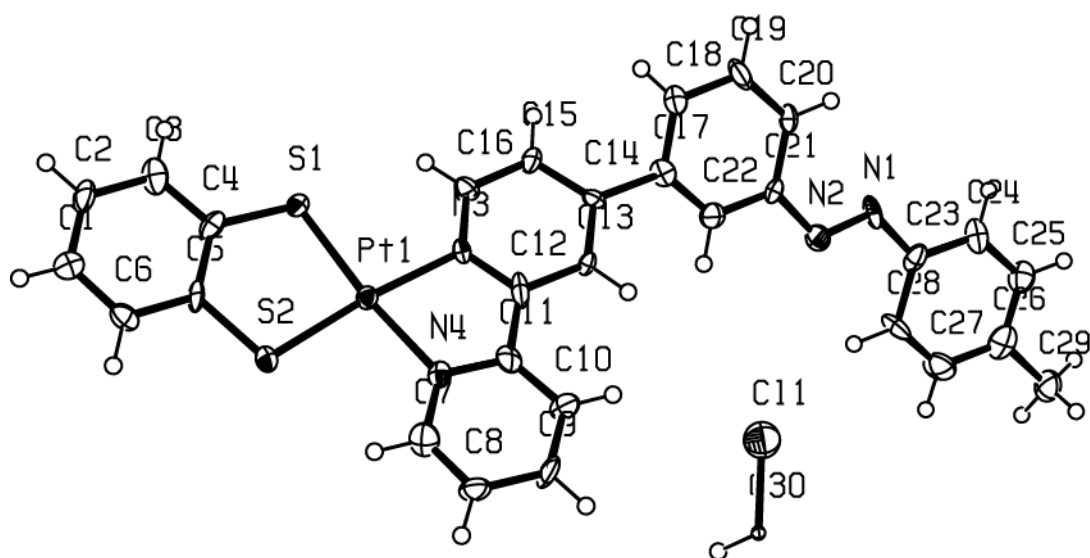


Fig. S2 An ORTEP drawing of complex **2** ( $C_{29}H_{22}N_4PtS_2 \cdot 0.5CH_2Cl_2$ ) with thermal ellipsoid set at the 50% probability level.

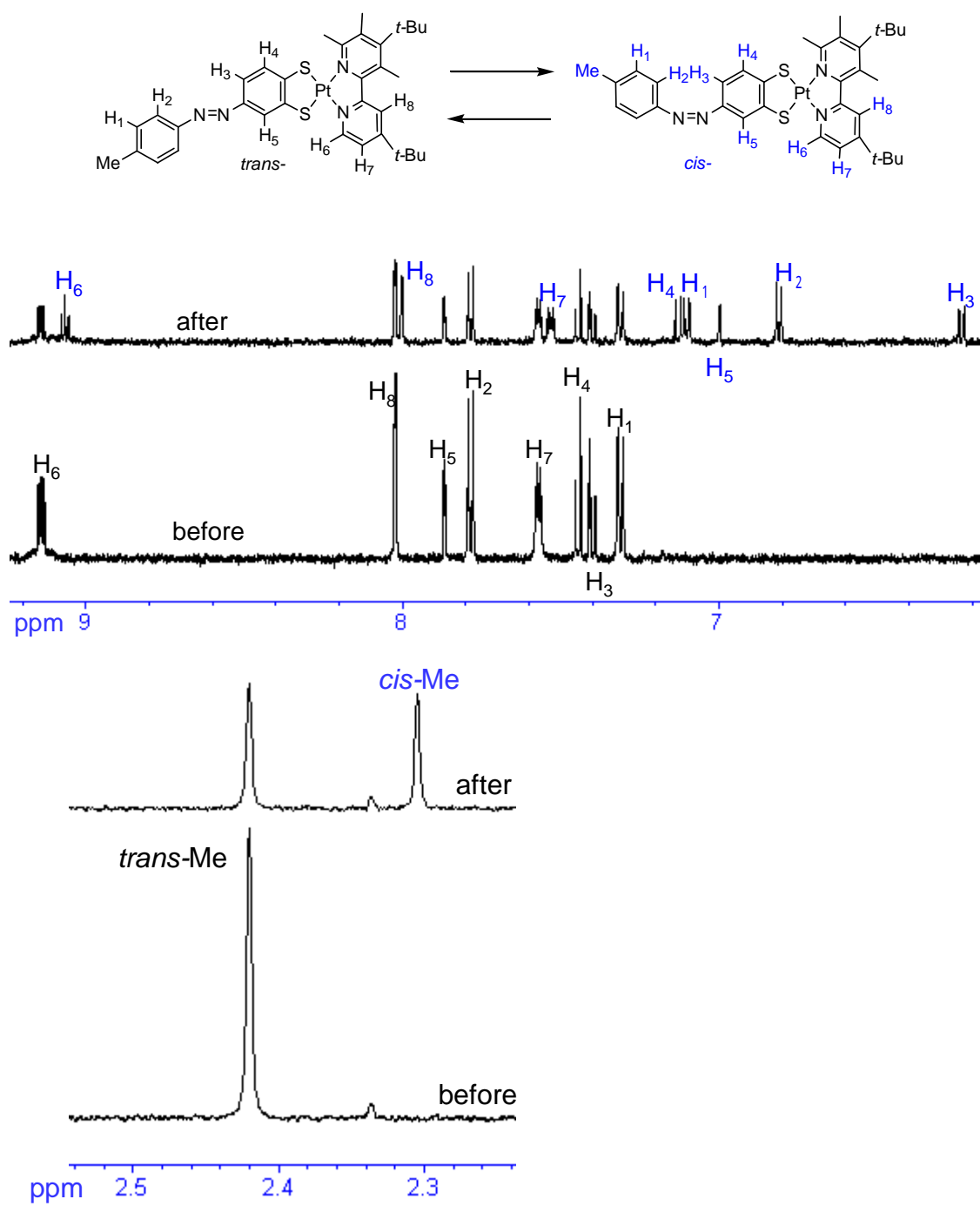


Fig. S3 <sup>1</sup>H-NMR spectra of complex **1** in dichloromethane-d<sub>2</sub> before and after irradiation with 405-nm light for 7.5 h.

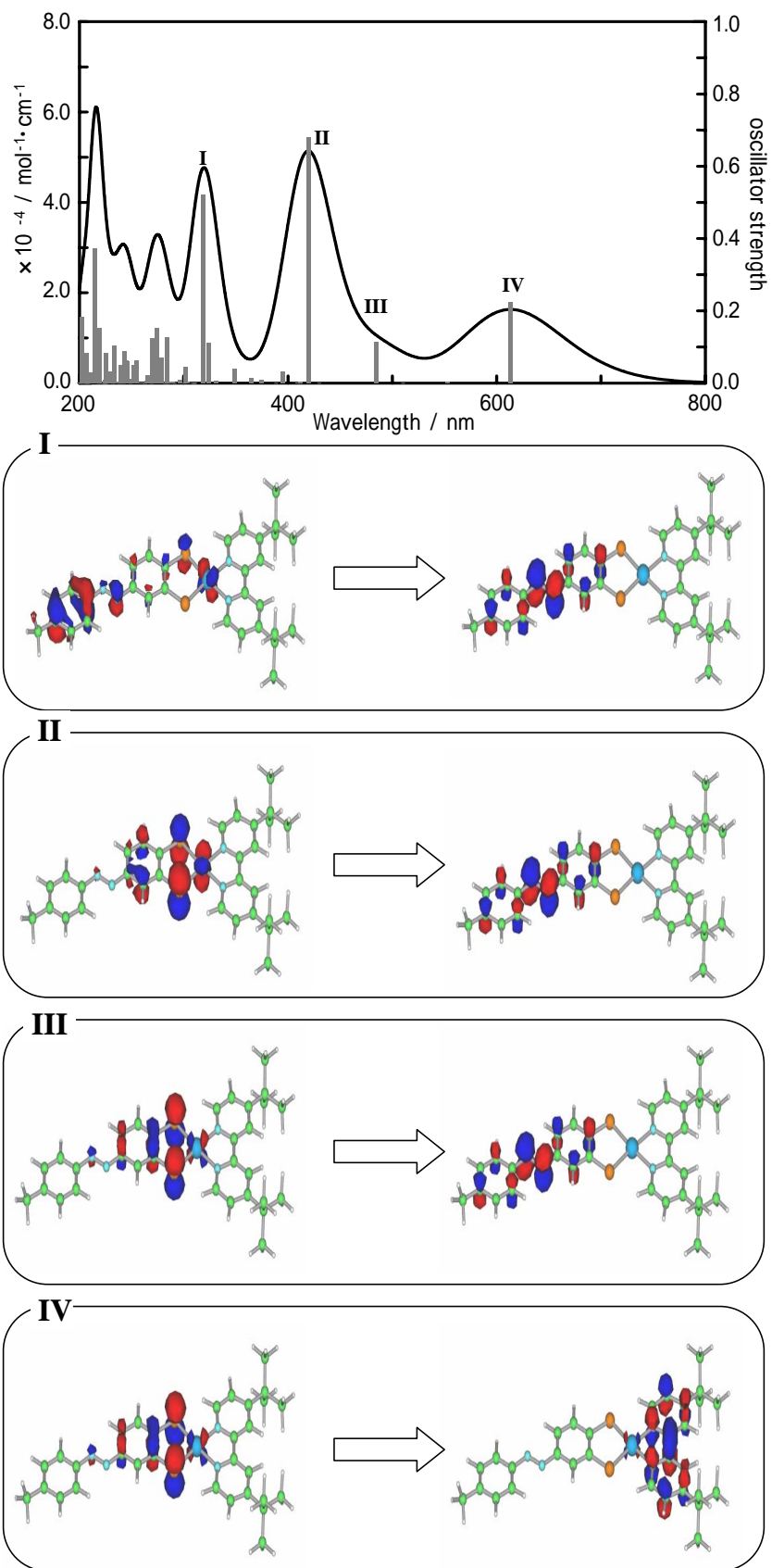


Fig. S4 An electronic spectrum of complex **1** and the main transitions in bands **I-IV** in dichloromethane calculated with TDDFT.

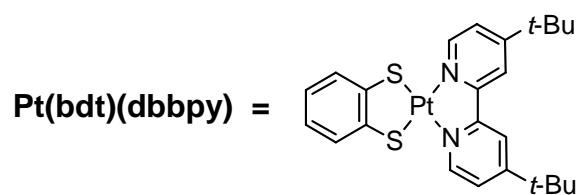
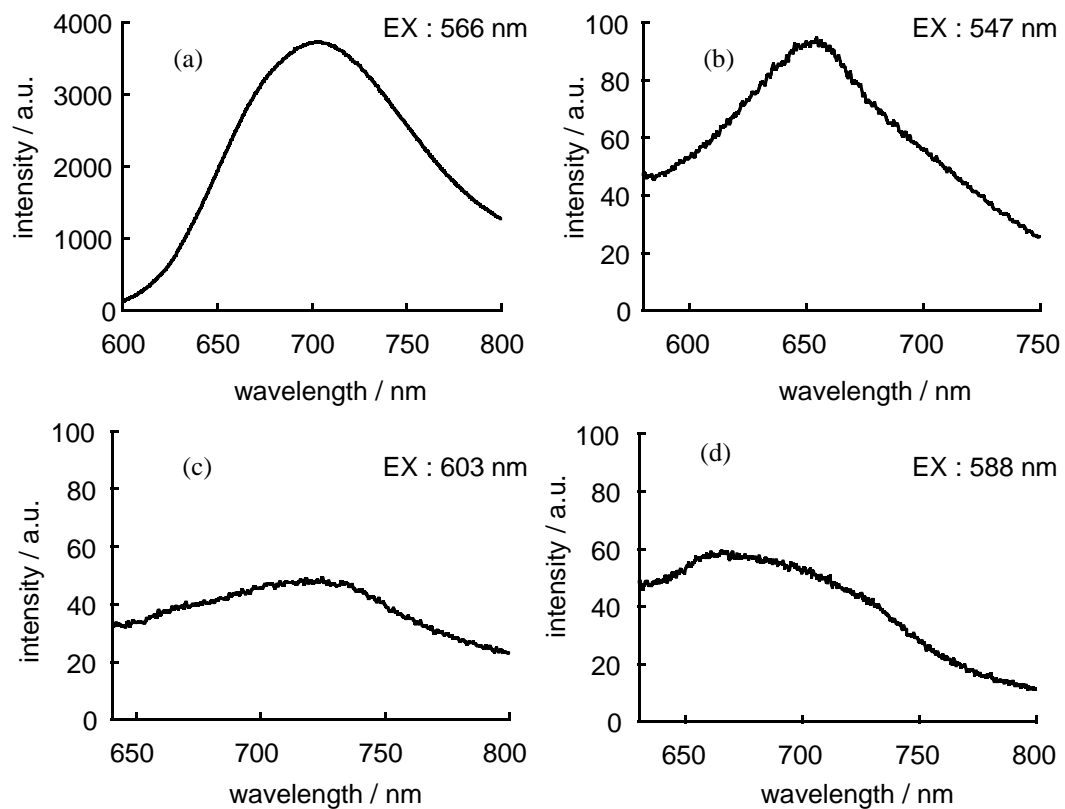


Fig. S5 Emission spectra of: (a) **Pt(bdt)(dbbpy)**, (b) **1**, (c) **2**, (d) **3** in dichloromethane at room temperature upon excitation of the MMLL'CT band.

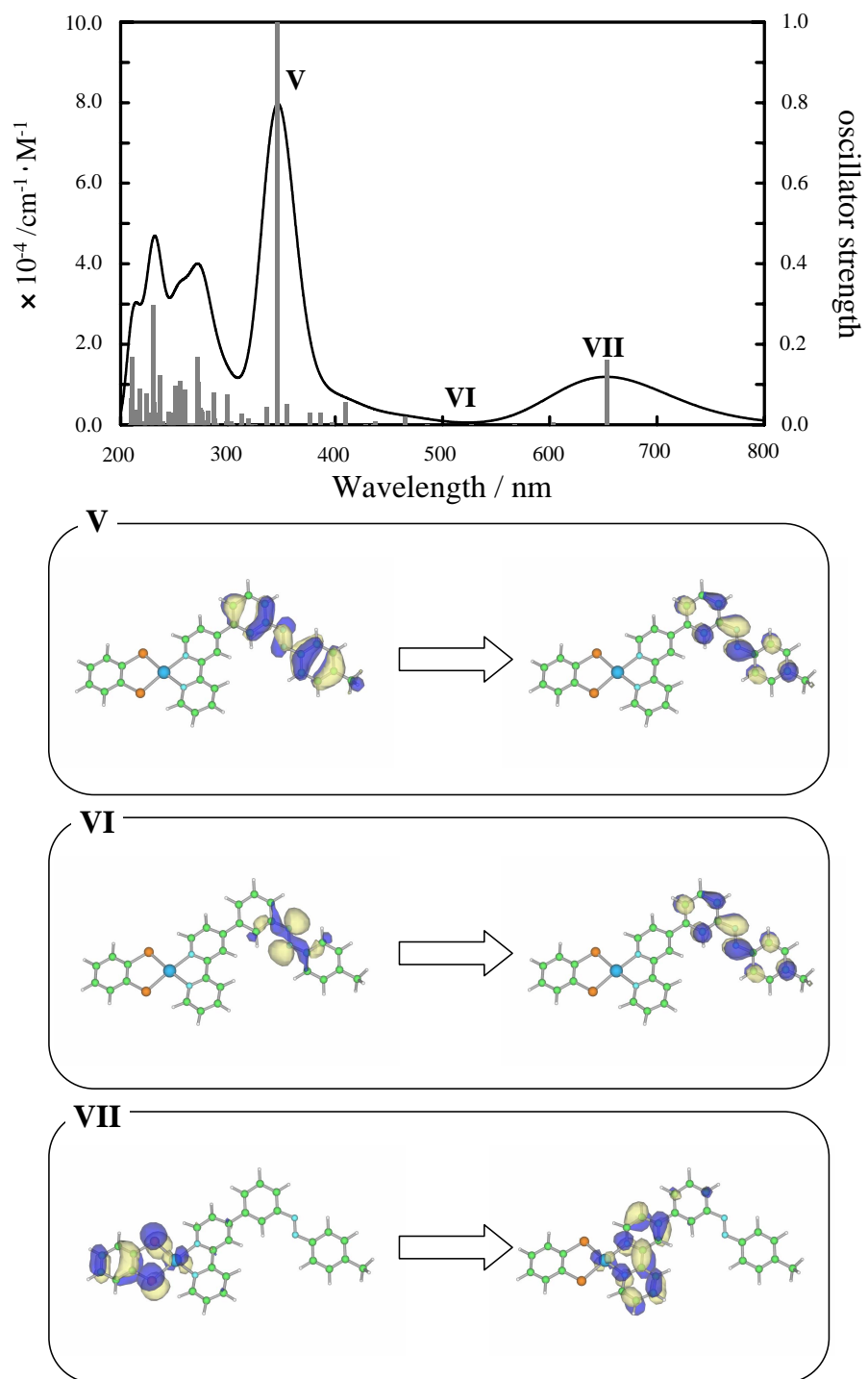


Fig. S6 An electronic spectrum of complex **2** and the main transitions in bands **V-VII** in dichloromethane calculated with TDDFT.

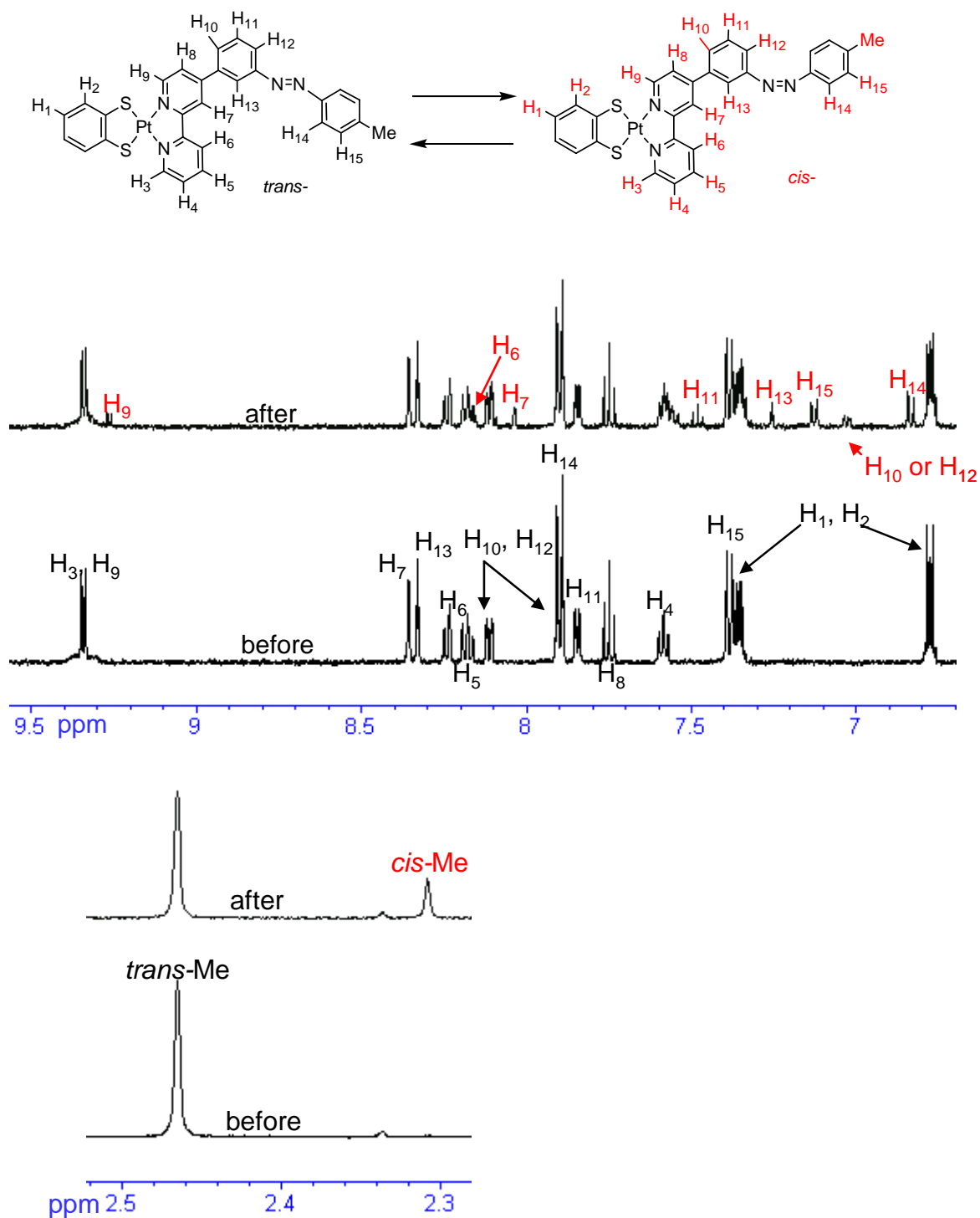


Fig. S7 <sup>1</sup>H-NMR spectra of complex **2** in dichloromethane-d<sub>2</sub> before and after irradiation with 365-nm light for 4 h.



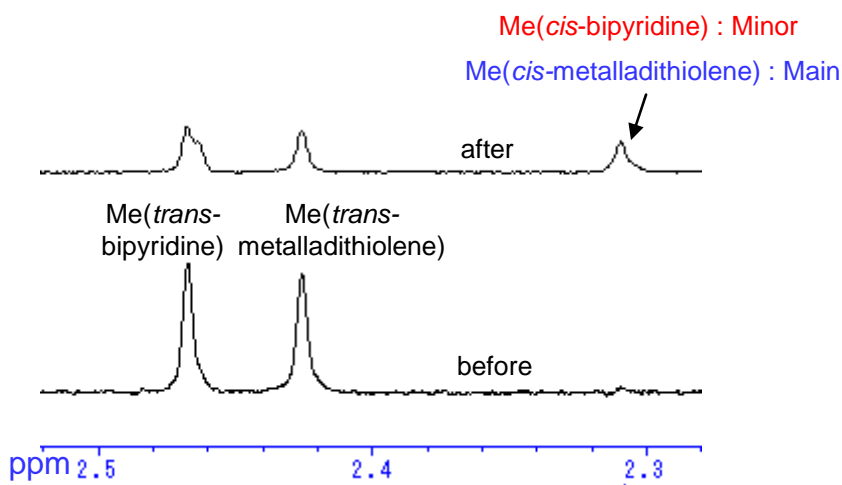
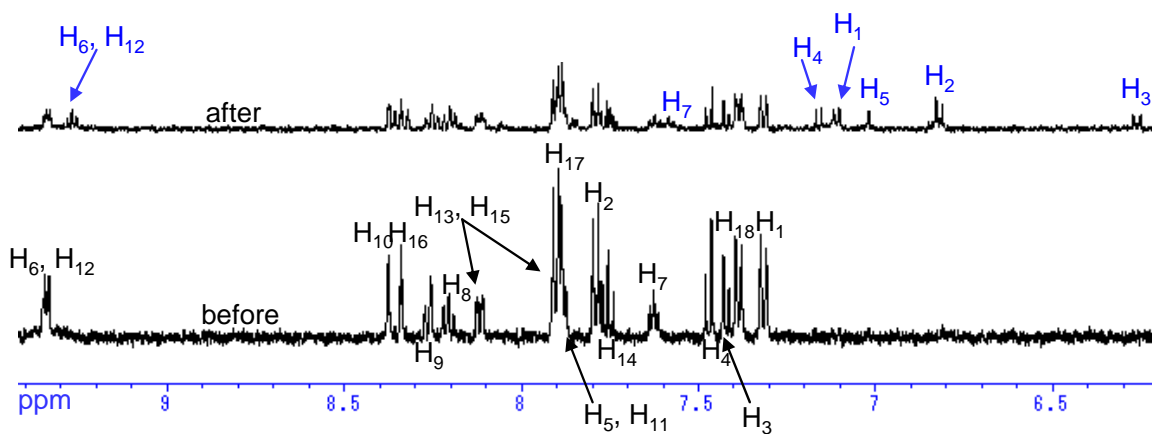
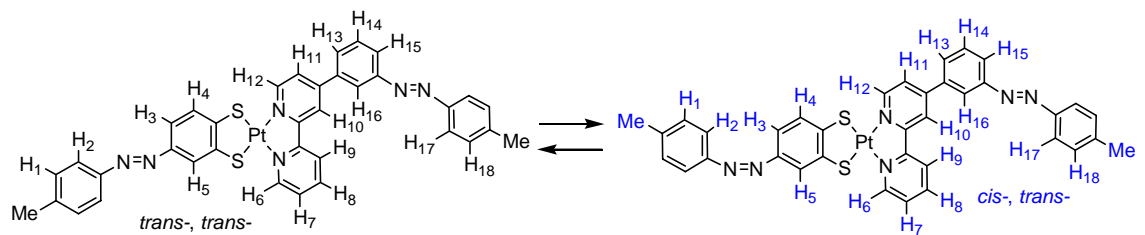


Fig. S8 <sup>1</sup>H-NMR spectra of complex **3** in dichloromethane-d<sub>2</sub> before and after irradiation with 405-nm light for 4 h.

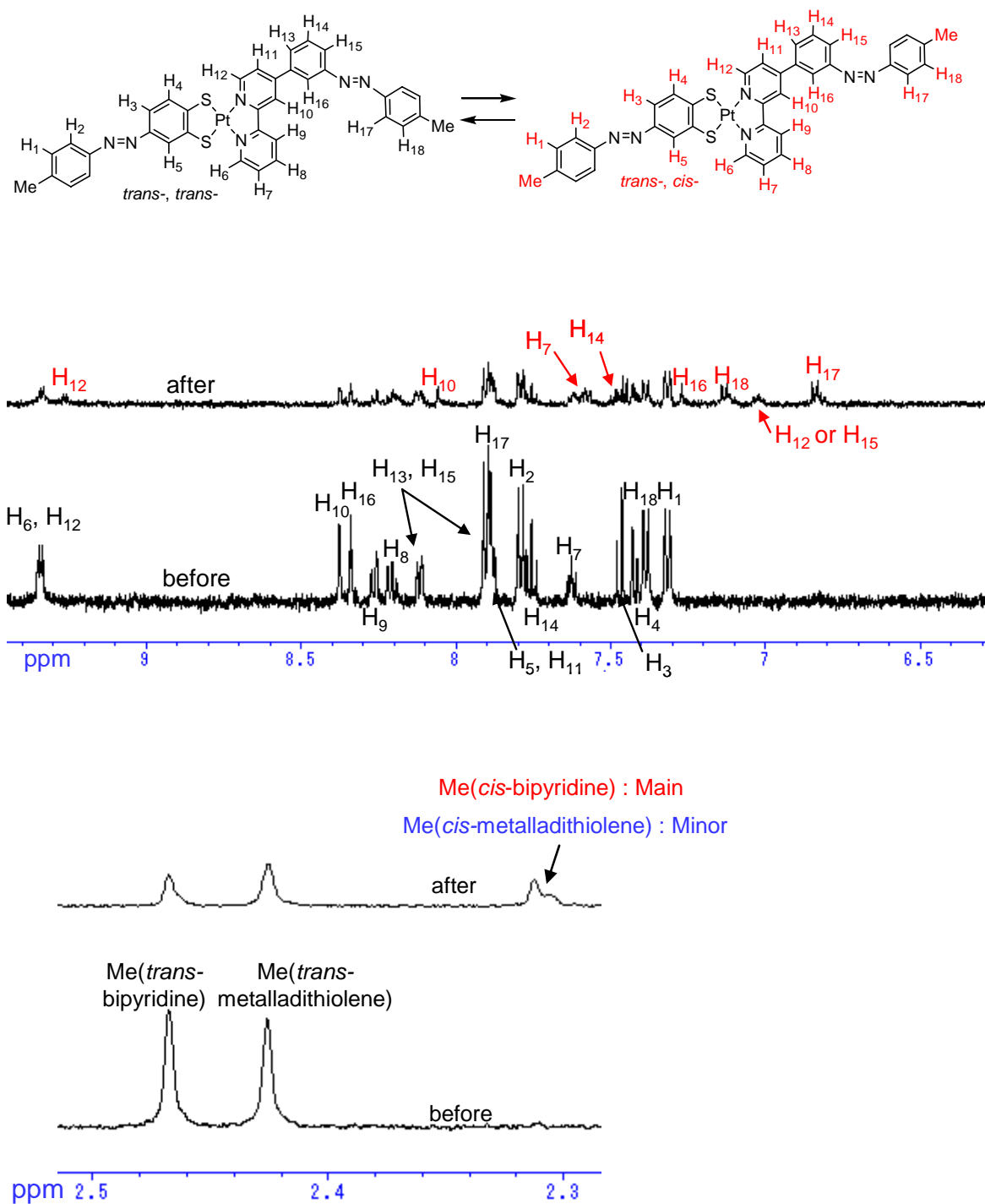
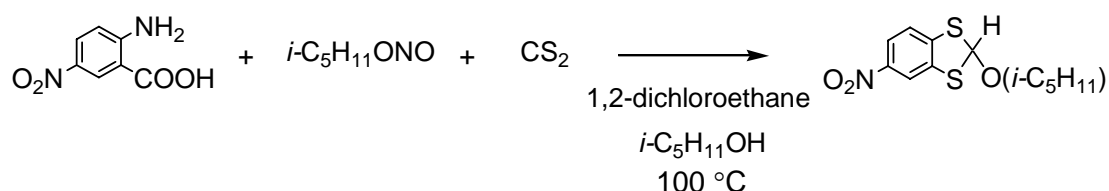


Fig. S9  $^1\text{H-NMR}$  spectra of complex **3** in dichloromethane- $d_2$  before and after irradiation of 365-nm light for 3.5 h.

## Experimental

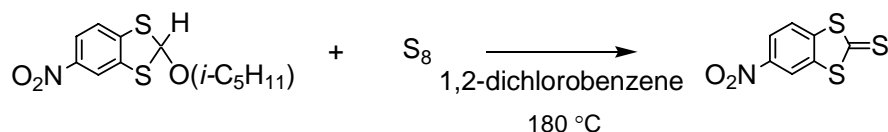
### 1) Syntheses

#### 2-Isoamyl-5-nitro-1,3-benzenedithiol (**4**)



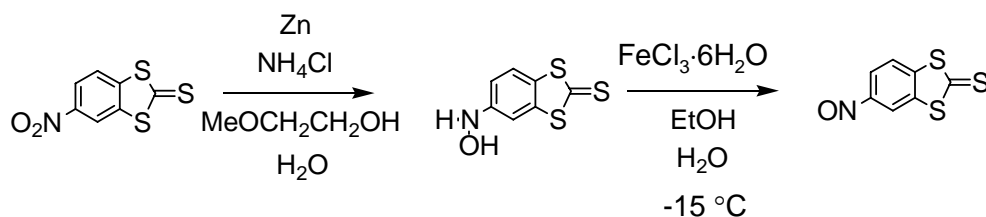
4-Nitroanthranilic acid (25 g, 0.14 mol),  $\text{CS}_2$  (70 ml, 1.2 mol) and  $i\text{-C}_5\text{H}_{11}\text{OH}$  (30 ml, 0.28 mol) were dissolved in 1,2-dichloroethane (300 mL). To this refluxing brown suspension, isopentyl nitrite (19 g, 0.16 mol) in 1,2-dichloroethane (500 mL) was added dropwise in 16 hours. After further 6-hour-reflux the reddish brown suspension was evaporated, and the residue was extracted with ether and washed with water. After drying with  $\text{Na}_2\text{SO}_4$  and evaporation, the reddish brown crude was purified by silica gel column chromatography with hexane-chloroform (1:1 v/v) as an eluent. Solvents in the eluent was evaporated to obtain **4** as reddish brown oil: yield; 13 g (31%).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  8.20 (d, (2.0), 1H), 7.96 (dd, (8.6, 2.1) 1H), 7.45 (d, (8.6), 1H), 6.90 (s, 1H), 3.42 (dt, (10, 3.4), 2H), 1.41 (dt, (9.8, 3.3), 2H), 1.01-0.95 (m, 1H), 0.84 (d, (6.8), 6H).

#### 5-Nitro-2-thioxo-1,3-benzenedithiole-2-thione (**5**)



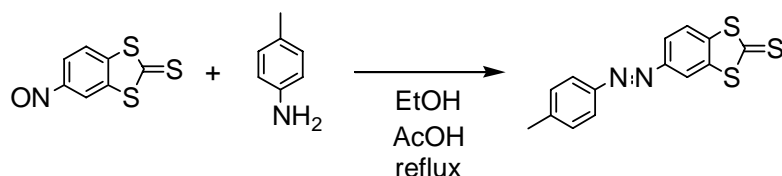
**4** (12 g, 43 mmol) and elemental S (1.6 g, 50 mmol) was dissolved in 1,2-dichlorobenzene (200 ml), and the red-brown solution was refluxed for 18 hours. After the evaporation of the solvent, the reddish black crude was purified by silica gel column chromatography, with hexane-chloroform (1:1 v/v) as an eluent. The eluent was evaporated and **5** was obtained as yellow-brown solid: yield; 4.8 g (49%).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  8.34 (d, (2.2), 1H), 8.24 (dd, (8.7, 1.9), 1H), 7.61 (d, (8.8), 1H).

### 5-Nitroso-2-thioxo-1,3-benzenedithiole-2-thione (6)



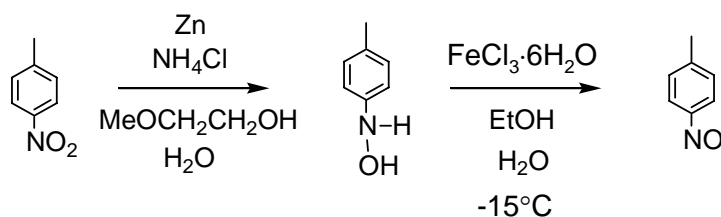
All manipulations were done under a nitrogen atmosphere. **5** (4.8 g, 21 mmol) and NH<sub>4</sub>Cl (2.5 g, 46 mmol) were dissolved in 2-methoxyethanol (550 mL) and water (34 mL). Into this suspension, 5.0 g of Zn powder (washed by dilute HCl) was added. After 4-hour stirring at room temperature, another Zn powder (0.44 g) was added and continued stirring for 1 hour. In another flask, FeCl<sub>3</sub>·6H<sub>2</sub>O was dissolved in water (320 mL) and EtOH (70 mL), remaining temperature to -15°C. The former suspension was filtrated and the obtained yellow-brown solution was added to the latter solution by dropwise in 6 hours. Then the yellow-brown suspension was added to cold water (600 mL) and filtered. Obtained brown solid **6** was washed with water and dried in vacuum, and used in the next reaction without further purification: yield; 3.96 g (88%). <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ 8.03(dd, (8.6, 1.8), 1H), 7.86(d, (1.6), 1H), 7.72(d, (8.8), 1H).

### 5-(*p*-Tolylazo)-1,3-benzodithiole-2-thione (7)



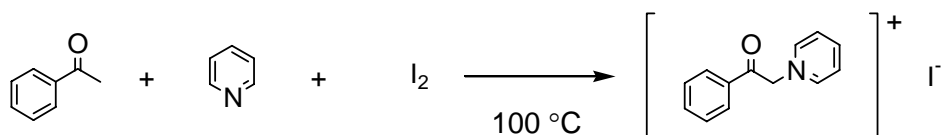
A suspension of **6** (3.96 g, 18 mmol) and *p*-toluidine (2.15 g, 20 mmol) in EtOH (640 mL) and AcOH (220 mL) was refluxed for 19 h with the colour change from yellow-brown to brown. Then the hot suspension was filtrated, and the filtrate was evaporated. Obtained dark-brown crude was purified by alumina column chromatography with hexane-chloroform (1 : 1 v/v) as an eluent. The orange fraction was evaporated to obtain **7** as red or orange solid: yield; 2.6 g (48%). <sup>1</sup>H-NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 8.04(d, (1.3), 1H), 7.98(dd, (8.6, 2.0), 1H), 7.84(d, (8.2), 2H), 7.64(d, (8.9), 1H), 7.35(d, (7.9), 1H), 2.44(s, Me).

### 4-Nitrosotoluene (8)



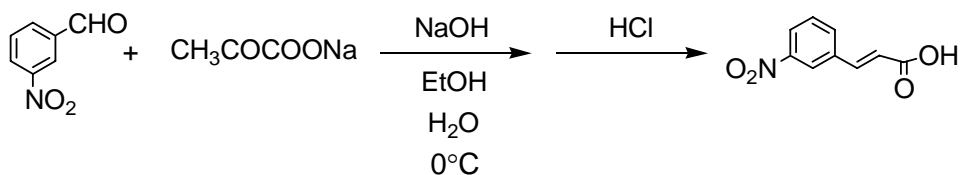
All manipulations were done under a nitrogen atmosphere. 4-Nitrotoluene (20 g, 0.15 mol) and  $\text{NH}_4\text{Cl}$  (12 g, 0.22 mol) were resolved in 2-methoxyethanol (360 mL) and water (100 mL). To this solution Zn powder (washed with dilute HCl) (26 g, 0.40 mol) was added. After stirring 2h, this exothermic reaction resulted in the colour change from yellow to pale yellow. Then another Zn powder (22 g, 0.34 mol) was added and stirred for 1h. The suspension was filtered and the pale yellow filtrate was poured into the drop funnel attached to the three-necked flask containing the water (640 mL) and EtOH (160 mL) solution of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (102 g, 0.37 mol). To the latter solution the former was added by dropwise in 6h at  $-15^\circ\text{C}$ , generating yellow precipitate. After finishing the addition, continuing stirring for 30 min and then to the suspension a sufficient amount of water was added as a poor solvent, then the yellow precipitate **8** was filtrated and washed with water: yield 14 g (77%).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$ 7.81 (d, (8.4), 2H), 7.39 (d, (8.6), 2H), 2.44 (s, Me).

## 2-Acetylpyridinepyridinium iodide (**9**)



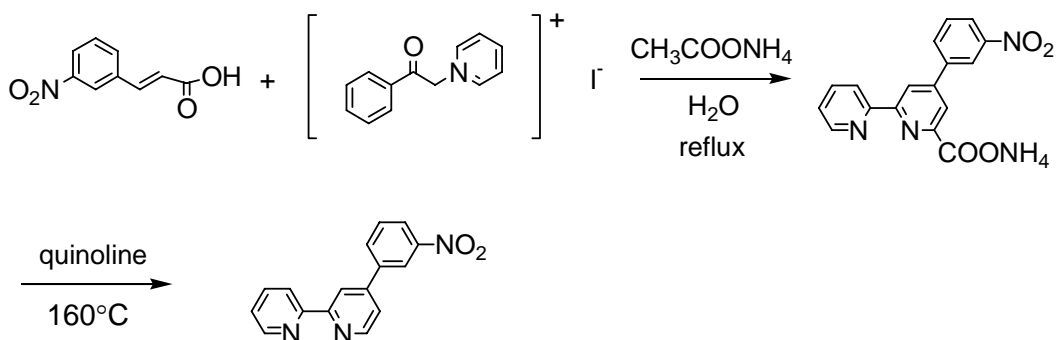
Under a nitrogen atmosphere, iodine (62 g, 0.24 mol) was added to the pyridine (210 ml, 2.6 mol). To the deep-purple suspension 2-acetylpyridine (90 ml, 0.80 mol) was added, then stirring at  $100^\circ\text{C}$ . After 1 hour the suspension was cooled to room temperature, then filtered the precipitate and washed with cold pyridine. The precipitate and a spoon of charcoal were poured into EtOH and refluxed for an hour. Then charcoal was removed by hot filtration and the filtrate was cooled in refrigerator to gain the precipitate. By filtration and wash with EtOH, dark yellow-green crystal of **9** was obtained: yield; 43 g (27%).

### 3-(3'-Carboxy-3'-oxo-1'-propenyl)nitrobenzene (**10**)



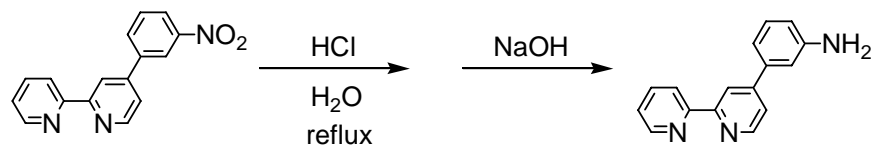
A suspension of *m*-nitrobenzaldehyde (14 g, 96 mmol) and sodium pyruvate (10 g, 95 mmol) was cooled to 0°C. To the suspension NaOH (2.4 g, 62 mmol) in water (50 mL) was added dropwise in 10 min. After continuous stirring for 2 hours, the resulting orange suspension was acidified to pH 2 with conc. HCl. The obtained yellow precipitate **10** was filtered and washed by water, then dried under vacuum: yield; 7.6 g (36 %). <sup>1</sup>H-NMR (DMSO-*d*<sub>6</sub>): δ 8.46. (s,1H), 8.22 (d, (8.1), 1H), 8.15 (d, (7.8), 1H), 7.70 (dd, (8.1, 8.1), 1H), 7.60 (d, (16), 1H), 7.08 (d, (16), 1H).

### 4-(3''-Nitrophenyl)-2,2'-bipyridine (**11**)



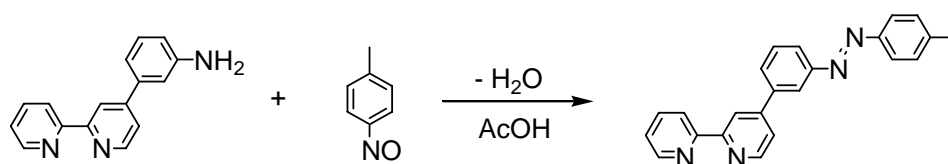
A mixture of **10** (7.6 g, 34 mmol), **9** (11 g, 34 mmol) and ammonium acetate (38 g, 49 mmol) in water (190 ml) was refluxed. The obtained white-brown solid was filtrated and washed with water until the filtrate becomes clear. After thorough dry under vacuum, the solid was dissolved in quinoline (20 mL), and then the black suspension was heated to 150°C. After removing quinoline under a reduced pressure, the black residue was purified by alumina column chromatography with CHCl<sub>3</sub> as a eluent. The white solid **11** was obtained by evaporating the eluent: yield; 4.4 g (47%). <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ 8.80 (d, (4.9), 1H), 8.73 (m, 2H), 8.62 (s, 1H), 8.48 (d, (8.4), 1H), 8.32 (d, (7.3), 1H), 8.10 (d, (7.8), 1H), 7.86 (ddd, (7.6, 7.6, 1.6), 1H), 7.70 (dd, (8.1, 8.1), 1H), 7.57 (dd, (5.4, 1.6), 1H), 7.36 (ddd, (7.3, 4.6, 1.2), 1H).

#### 4-(3''-Anilino)-2,2'bipyridine (**12**)



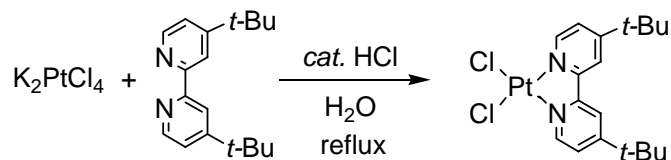
**11** (4.4 g, 16 mmol) was dissolved in conc. HCl (50 mL). To the solution a suspension of SnCl<sub>2</sub>·2H<sub>2</sub>O (15 g, 67 mmol) in water (100 mL) was added by dropwise in 30 min. After stirring for 1h, the solution turning to pale yellow suspension, another portion of SnCl<sub>2</sub>·2H<sub>2</sub>O (8.1 g, 36 mmol) in water (50 mL) was added. Then the suspension was refluxed for 1.5h. After adding conc. HCl (13 mL), the suspension was again refluxed for 2h. Then the suspension was alkalinized with NaOH to obtain orange precipitate. The precipitate was filtered, and extracted with AcOEt. After removing the AcOEt, the residue was extracted again with CHCl<sub>3</sub> and evaporated the solvent to obtain pale yellow solid of **12**: yield; 3.1 g (78%). <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ 8.71 (m, 2H), 8.63(d, (1.1),1H), 8.45(d, (7.8), 1H), 7.84(ddd, (7.8, 1.9), 1H), 7.51(dd, (5.4 Hz, 2.2 Hz, 1H), 7.33(dd, (7.6, 5.1), 1H), 7.28(dd, (7.6, 7.6), 1H), 7.15 (d, (7.8), 1H), 7.09 (s, 1H), 6.77 (d, (7.8), 1H).

#### 4-(3''-(4'''-Toluazo)phenyl)-2,2'bipyridine (*m*-azobpy, **13**)



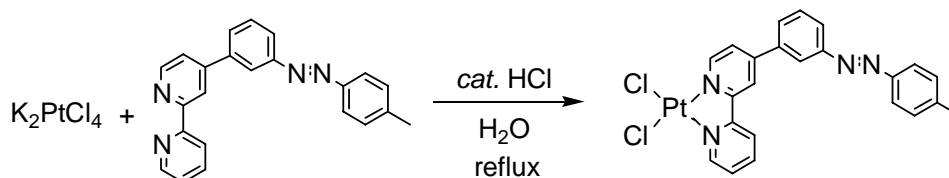
A mixture of **12** (3.0 g, 12 mmol) and **8** (5.1 g, 42 mmol) in AcOH (45 mL) was stirred for 2 days. The dark-orange suspension was neutralized with NaOH to obtain a reddish black precipitate, and it was extracted with CH<sub>2</sub>Cl<sub>2</sub>. After removing the solvent, the crude was purified by alumina column chromatography with CHCl<sub>3</sub> and hexane (1/1, v/v) as an eluent. Recrystallization from EtOH gave orange crystals of **13**: yield; 0.82 g (19%). <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ 8.77(d, (3.0), 1H), 8.76(s, 1H), 8.73(d, (7.6), 1H), 8.48(d, (8.1), 1H), 8.31(s, 1H), 7.99(d, (7.8), 1H), 7.89-7.82(m, 3H), 7.65(dd, (7.6, 7.6) 1H), 7.64(d, (4.9), 1H), 7.37-7.32 (m, 2H), 2.46 (s, 3H).

### PtCl<sub>2</sub>(4,4'-di-*t*-butylbipyridine) (PtCl<sub>2</sub>(dbbpy), **14**)



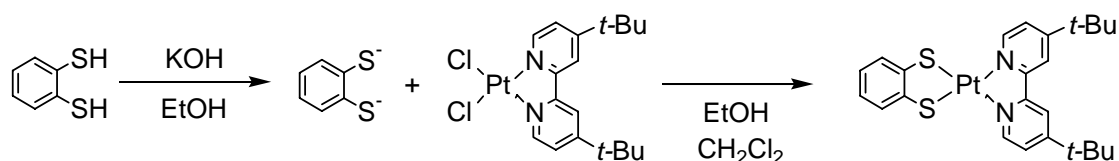
K2PtCl4 ( 406 mg, 0.96 mmol ) was dissolved in minimum amount of water. To the red solution several drops of conc. HCl and 4,4'-di-*tert*-butylbipyridine (258 mg, 0.96 mmol) were added. The red suspension was refluxed for 1 day, with the colour change to yellow. The yellow precipitate was filtered and washed with water, ether and hexane to obtain yellow powder of **14**. It was used in the next step without further purification because of insolubility: yield; 465 mg (91%). <sup>1</sup>H-NMR (CD<sub>2</sub>Cl<sub>2</sub>) : δ 9.57 (d, (6.3), 2H), 7.89 (d, (2.0), 2H), 7.58 (dd, (6.3, 2.3), 2H), 1.43 (s, *t*-Bu).

### PtCl<sub>2</sub>(*m*-azobpy) (**15**)



K2PtCl4 (424 mg, 1.0 mmol) was dissolved in minimum amount of water. To the solution several drops of conc. HCl and **13** (349 mg, 1.0 mmol) were added. The orange suspension was refluxed for 1 day. The resulting brown suspension was filtrated, washed with water, ether and hexane to obtain brown powder of **15**. It was used in the next step without further purification because of insolubility: yield; 596 mg (97%).

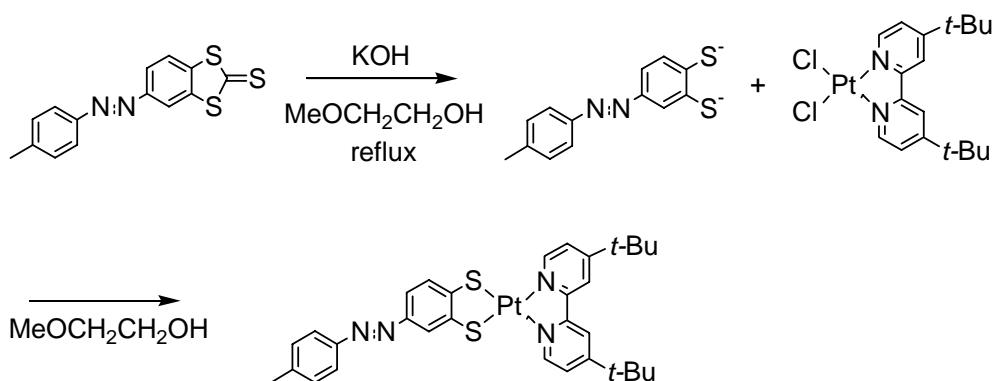
### Pt(bdt)(dbbpy) (**16**)





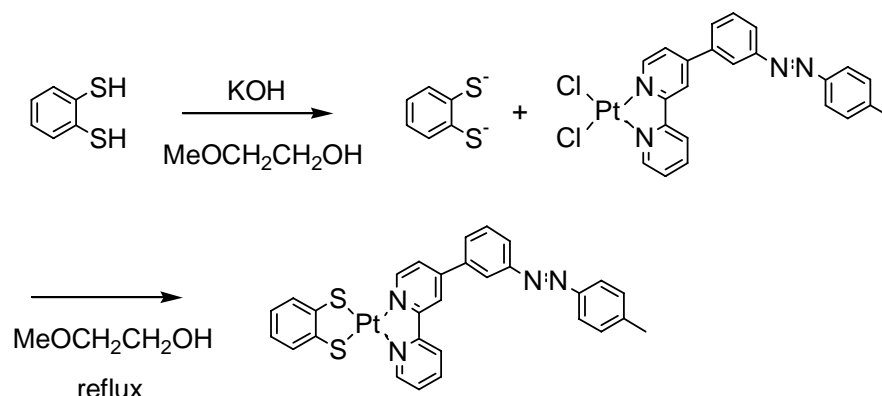
To a suspension of **14** (237 mg, 0.44 mmol) in CH<sub>2</sub>Cl<sub>2</sub>, an ethanol solution of KOH (350 mg, 6.25 mmol) and 1,2-benzenedithiol (130 mg, 0.91 mmol) was added through a bridge. The mixture immediately turned from yellow to dark-purple suspension. It was stirred for 1 day, shielded against the light. Then it was extracted with CH<sub>2</sub>Cl<sub>2</sub>, washed with sat. NaCl<sub>aq</sub>. After evaporation, the residue was purified by silica gel column chromatography with CH<sub>2</sub>Cl<sub>2</sub> as a eluent. The first purple fraction was collected, evaporated and reprecipitated from CH<sub>2</sub>Cl<sub>2</sub> and hexane to obtain purple solid of **16**: yield; 126 mg (47%). <sup>1</sup>H-NMR (CD<sub>2</sub>Cl<sub>2</sub>) : δ 9.14 (d, (6.6), 2H), 8.00 (d, (2.0), 2H), 7.54 (dd, (6.1, 2.1), 2H), 7.33-7.28 (m, 2H), 6.76-6.72 (m, 2H), 1.44 (s, *t*-Bu). Anal. Calcd for C<sub>24</sub>H<sub>28</sub>N<sub>2</sub>PtS<sub>2</sub>: C, 47.75; H, 4.67; N, 4.64. Found: C, 47.91; H, 4.72; N, 4.34.

### Pt(azobdt)(dbbpy) (complex **1**)



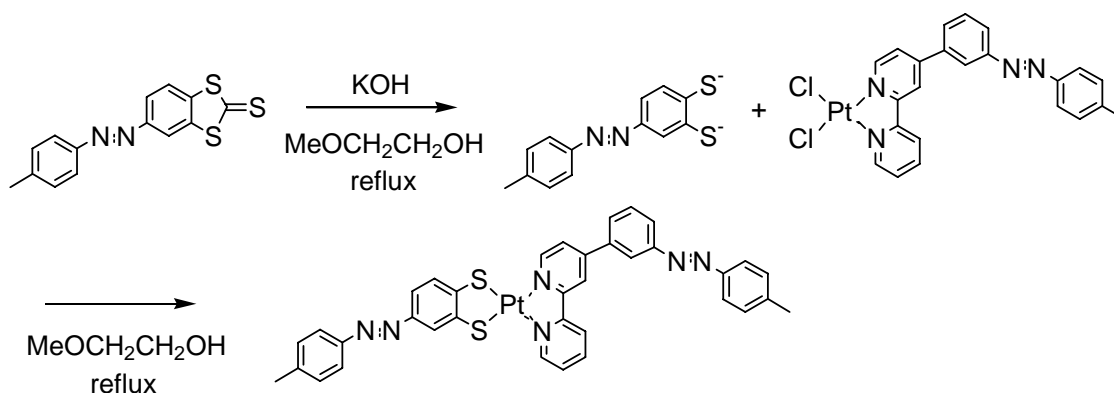
To an orange solution of **7** (501 mg, 1.6 mmol) in 2-methoxyethanol (150 mL) KOH (463mg, 8.0 mmol) was added. Then the mixture was refluxed for 1 hour, gradually turning to a reddish black suspension. After the suspension was cooled to r.t., **14** (667 mg, 1.2 mmol) was added to the suspension. The mixture was stirred for 1 day, shielded from light. After evaporation of the solvent, the reddish-black residue was extracted with CH<sub>2</sub>Cl<sub>2</sub>, washed with sat. NaCl<sub>aq</sub>, then purified by basic alumina column chromatography with CH<sub>2</sub>Cl<sub>2</sub> as an eluent. Recrystallization from acetonitrile and dichloromethane gave dark-red crystals of complex **1**: Yield; 400 mg (46%). <sup>1</sup>H-NMR (CD<sub>2</sub>Cl<sub>2</sub>) : 9.14 (d, (6.1), 1H), 9.14 (d, (6.4), 1H), 7.87 (d, (2.0), 1H), 7.78 (d, 8.4), 7.58 (dd, (2.3, 2.3), 1H), 7.56 (dd, (2.3, 2.3), 1H), 7.44 (d, (8.6), 1H), 7.40 (dd, (8.4, 1.8), 1H), 7.31 (d, 2H), 2.42 (s, Me), 1.45 (s, *t*-Bu). Anal. Calcd for C<sub>31</sub>H<sub>34</sub>N<sub>4</sub>PtS<sub>2</sub>: C, 51.58; H, 4.75; N, 7.76. Found: C, 51.40; H, 4.86; N, 7.64.

### Pt(bdt)(*m*-azobpy) (complex 2)



KOH (105 mg, 1.9 mmol) was dissolved in hot 2-methoxyethanol (60 mL). To the solution 1,2-benzenedithiol (91 mg, 0.59 mmol) was added. To the slightly yellow solution **15** (350 mg, 0.57 mmol) was added, and then the solution rapidly turned to blue-purple. After refluxing for 30 min with shielding light, the reaction mixture was evaporated, and the residue was purified by basic alumina column chromatography with CH<sub>2</sub>Cl<sub>2</sub> as an eluent. Recrystallization from acetonitrile and dichloromethane gave dark-purple crystals of complex **2**: yield; 196 mg (50%). <sup>1</sup>H-NMR (CD<sub>2</sub>Cl<sub>2</sub>) : δ 9.34 (d, (5.6), 2H), 8.35 (d, (1.7), 1H), 8.32 (dd, (1.7, 1.7), 1H), 8.23 (d, (7.8), 1H), 8.17 (ddd, (7.8, 7.8, 1.5), 1H), 8.11(ddd, (8.0, 1.8, 1.1), 1H), 7.90-7.88 (m, 3H), 7.84 (dd, (5.9, 2.0), 1H), 7.74(dd, (7.8, 7.8), 1H), 7.58(ddd, (7.3, 5.7, 1.5), 1H), 7.38(d, (8.1), 2H), 7.36-7.33(m, 2H), 6.79-6.75 (m, 2H), 2.46 (s, Me). Anal. Calcd for C<sub>29</sub>H<sub>22</sub>N<sub>4</sub>PtS<sub>2</sub>·0.5CH<sub>2</sub>Cl<sub>2</sub>: C, 48.66; H, 3.18; N, 7.69. Found: C, 48.30; H, 3.31; N, 7.35.

### Pt(azobdt)(*m*-azobpy) (complex 3)



To an orange solution of **7** (153 mg, 0.51 mmol) in 2-methoxyethanol (60 mL) KOH (140 mg, 2.5 mmol) was added and then the mixture was refluxed for 3 hours

with shielding light. The solution changed to reddish black suspension. To the suspension **15** (310 mg, 0.50 mmol ) was added and then the mixture was refluxed again for 1 hour. The mixture was evaporated, and the brownish black residue was purified with basic alumina column chromatography with CH<sub>2</sub>Cl<sub>2</sub> as an eluent. Black solid of complex **3** was obtained from reprecipitation from and acetonitrile and dichloromethane: yield; 88 mg (22%). <sup>1</sup>H-NMR (CD<sub>2</sub>Cl<sub>2</sub>) : δ 9.33-9.31 (m, 2H), 8.36 (d, (1.7), 1H), 8.33 (brs, 1H), 8.25 (d, (7.8), 1H), 8.19 (dd, (7.2, 7.2), 1H), 8.11 (d, (8.0), 1H), 7.90 (d, (8.3), 2H), 7.87-7.86 (m, 3H), 7.79 (d, (8.0), 2H), 7.74 (dd, (7.7, 7.7), 1H), 7.61 (ddd, (5.7, 5.7, 1.7), 1H), 7.46 (dd, (8.3, 1.2), 1H), 7.41 (dd, (8.4, 1.8), 1H), 7.38 (d, (7.8), 2H), 7.31 (d, (7.8), 2H), 2.46 (s, Me), 2.42 (s, Me). Anal. Calcd for C<sub>36</sub>H<sub>28</sub>N<sub>6</sub>PtS<sub>2</sub>: C, 53.79; H, 3.51; N, 10.45. Found: C, 53.61; H, 3.62; N, 10.20.

## 2) Supply of monochromic light

Monochromic light was supplied by a high-pressure mercury lamp (Ushio Electronic Inc.). The bright lines were splitted by a monochromator (Jasco CT-10T).

## 3) DFT calculations

In the DFT calculations, the three-parameterized Becke-Lee-Yang-Parr (B3LYP) hybrid exchange-correlation functional was employed. For comparisons with the UV-vis spectra observed in dichloromethane, the solvent effect was considered with the polarized continuum model (PCM). As basis sets, 6-31G was chosen for C, H, N, and S, and Lanl2DZ (Hay-Wadt ECP) for Pt. The geometries of complexes **1** and **2** were optimized by the DFT(B3LYP) method with the solvent effect.

## 4) Preparation of samples for UV-vis and NMR spectroscopy upon irradiation with monochromic light

Since the isomerization behaviour of the azobenzene moiety on the metalladithiolene side was extremely subject to protic impurities, triethylamine (1 eq *v.s.* complex) was added to samples for UV-vis spectroscopy, and calcium hydride or potassium *tert*-butoxide was suspended in those for NMR spectroscopy, as proton scavengers. Decomposition of the complexes was not at all observed in all measurements by addition of these proton scavengers.