Supplementary information

Uni- and bi-directional light-induced switching of diarylethenes on gold nanoparticles

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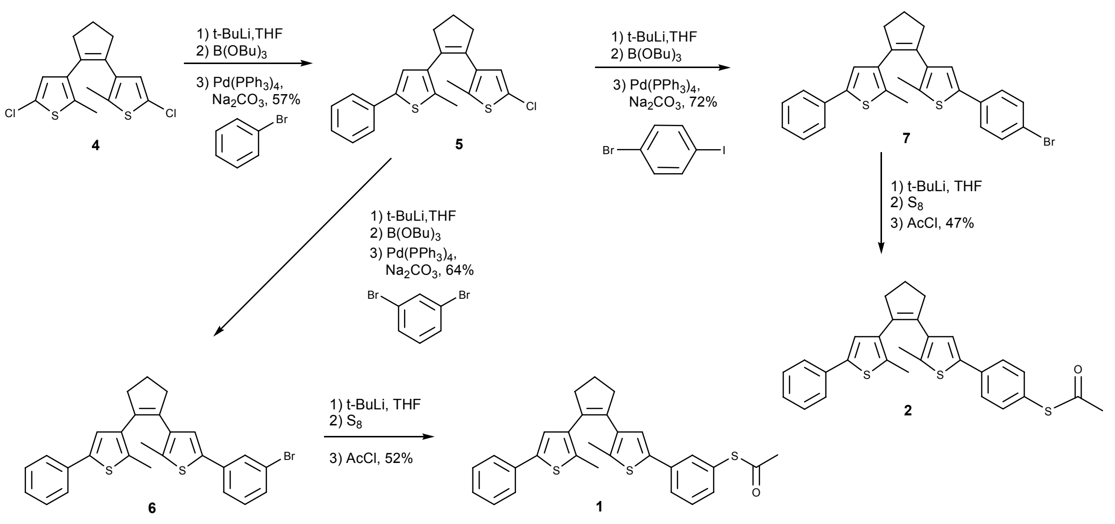
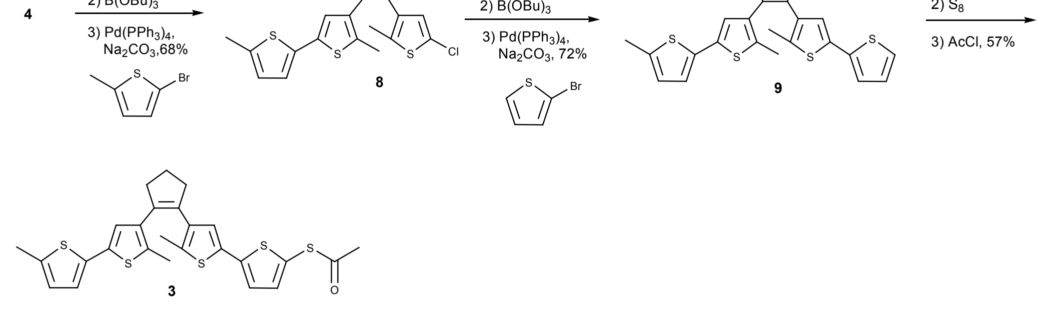
Synthesis:

The synthetic strategy for the preparation of compounds **1**, **2** and **3** was based on a series of palladium catalysed cross-coupling reactions starting from the known 1,2-bis(5-chloro-2-methylthien-3-yl)cyclopentene **4** [1]**.** The final products **1**, **2** and **3** were synthesised by treatment of **6**, **7** and **9** with n-butyllithium followed by the addition of sulphur and the protection with acetyl chloride giving moderated yields.





Reagents and starting materials were used as obtained from Aldrich and Acros Chimica. ^{1}H NMR were recorded on a Varian VXR-300 spectrometer (at 300 MHz) at ambient temperature. ^{13}C NMR were recorded on a Varian VXR-300 (at 75.4 MHz). Chemical shifts are denoted in δ (ppm) referenced to the residual $CHCl_3$ peaks. Coupling constants J, are denoted in Hz. Mass spectra were recorded with a MS-Jeol mass spectrometer with ionisation according to EI^+ procedure. Aldrich, silica gel, Merck grade 9385, (230-400 mesh) was used for column chromatography. The solvent were distilled and dried before use, if necessary, using standard methods.

1-(5-Chloro-2-methylthien-3-yl)-2-(2-methyl-5-phenylthien-3-yl)cyclopentene (5):

To a solution of compound **4** (2.25 g, 6.83 mmol) in THF (100 mL), kept under an inert N_2 atmosphere, t-BuLi (4.70 mL of 1.6 M solution in hexane, 7.51 mmol) was added. After 1h, $B(OBu)_3$ (2.77 mL, 10.3 mmol) was added and the mixture was stirred for 1h to produce a boronic ester intermediate. In a separate flask bromobenzene (2.86 mL, 13.66 mmol), $Pd(PPh_3)_4$ (0.237 g, 0.21 mmol), THF (23 mL), 2M Na_2CO_3(aq.) (18 mL) and ethylene glycol (20 drops) were preheated to 80 ^{o}C and the boronic ester solution was added slowly. The reaction mixture was heated under reflux overnight, diluted with diethyl ether (200 mL) and washed with water (200 mL). The water layer was washed with an additional volume of ether (200 mL) and the combined organic phases were dried over Na_2SO_4 and concentrated. Subsequent chromatography on silica gel (hexane) afforded compound **5** as a sticky oil (1.95 g, 77 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 1.94 (s, 3H), 2.05 (s, 3H), 2.08-2.16 (m, 2H), 2.78-2.89 (m, 4H), 6.68 (s, 1H), 7.05 (s, 1H), 7.30 (t, J = 7.0 Hz, 1H), 7.37-7.42 (m, 2H), 7.55 (d, J = 7.3 Hz, 2H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ_C 14.1 (q), 14.3 (q), 22.9 (t), 38.4 (t), 38.5 (t), 123.8 (d), 125.0 (s), 125.3 (d), 126.8 (d), 127.0 (d), 128.8 (d), 133.2 (s), 133.7 (s), 134.4 (s), 135.1 (s), 135.3 (s), 136.3 (s), 139.8 (s) ppm. ; MS (EI): 370 [M^+]; HRMS: calcd. for $C_{21}H_{19}S_2Cl$ 370.062, found 370.063.

1-[5-(3-Bromophenyl)-2-methylthien-3-yl]-2-(2-methyl-5-phenylthien-3-yl)cyclopentane (6):

To a solution of compound **5** (1 g, 2.70 mmol) in THF (35 ml), kept under an inert N_2 atmosphere, t-BuLi (2.13 ml of 1.5 M solution in pentane, 3.20 mmol) was added. After 1h, $B(OBu)_3$ (1.09 ml, 4.05 mmol) was added and the mixture was stirred for 1h to produce a boronic ester intermediate. In a separate flask 1,3-dibromobenzene (0.653 ml, 5.40 mmol), $Pd(PPh_3)_4$ (0.094 g, 0.081 mmol), THF (15 ml), (aq.) 2M Na_2CO_3 (10 ml) and ethylene glycol (15 drops) were preheated to 80 ^{o}C and the boronic ester solution was added slowly. The reaction mixture was heated under reflux overnight, diluted with diethyl ether (200 ml) and washed with water (200 ml). The water layer was washed with an additional volume of ether (200 ml) and the combined organic phases were dried over Na_2SO_4 and concentrated. Subsequent chromatography on silica gel (hexane) afforded compound **6** as a sticky oil (0.88 g, 66 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.01 (s, 6H), 2.08-2.13 (m, 2H), 2.84-2.89 (m, 4H), 7.05 (s, 1H), 7.06 (s, 1H), 7.16-7.26 (m, 2H), 7.32-7.42 (m, 4H), 7.52 (d, J=7.3 Hz, 2H), 7.66 (s, 1H) ppm. ^{13}C NMR (75.4, $CDCl_3$): δ = 14.4 (q), 14.4 (q), 23.0 (t), 38.4 (t), 122.9 (s), 123.8 (d), 123.9 (d), 124.8 (d), 125.3 (d), 127.0 (d), 128.1 (d), 128.7 (d), 129.7 (d), 130.2 (d), 134.3 (s), 134.4 (s), 135.0 (s), 135.4 (s), 136.5 (s), 136.8 (s), 137.8 (s), 139.8 (s) ppm. HRMS: calcd. for $C_{27}H_{23}S_2Br$ 490.042, found 490.032.

1-[5-(3-Acetylsulfanylphenyl)-2-methylthien-3-yl]-2-(2-methyl-5-phenylthien-3-yl)cyclopentane (1):

Compound **6** (584 mg, 1.188 mmol) was dissolved in THF (25 ml) and the solution was cooled to -80 ^{o}C. To this solution was added dropwise t-BuLi (0.87 ml of 1.5 M solution in pentane, 1.307 mmol). After 2h S_8 (38 mg, 1.188mmol) dissolved in THF (2 ml) was added and the mixture was allowed to reach slowly room temperature. After 2h the reaction mixture was cooled to 0 ^{o}C and acetyl chloride (0.17 ml, 2.376 mmol) was added. After 3h the mixture was diluted with dichloromethane, washed with water and the organic phase dried (Na_2SO_4) and concentrated. Subsequent chromatography (hexane / dichloromethane 7:2) afforded compound **1** (301 mg, 52 %) as a sticky oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.99 (s, 3H), 2.00 (s, 3H), 2.05-2.15 (m, 2H), 2.43 (s, 3H), 2.85 (t, *J*=7.3 Hz, 4H), 7.04 (s, 1H), 7.06 (s, 1H), 7.20-7.40 (m, 5H), 7.48-7.56 (m, 4H) ppm. ^{13}C NMR (75.4, $CDCl_3$): δ = 14.4 (q), 23.0 (t), 30.2 (q), 38.5 (t), 123.9 (d), 124.7 (d), 125.3 (d), 126.3 (d), 126.9 (d), 128.5 (s), 128.8 (d), 129.5 (d), 131.0 (d), 132.7 (d), 134.4 (s), 134.5 (s), 134.9 (s), 135.2 (s), 135.7 (s), 136.6 (s), 136.8 (s), 138.3 (s), 139.7 (s), 193.8 (s) ppm. HRMS: calcd. for $C_{29}H_{26}OS_3$ 486.115, found 486.114.

1-[5-(4-Bromophenyl)-2-methylthien-3-yl]-2-(2-methyl-5-phenylthien-3-yl)cyclopentane (7):

To a solution of compound **5** (1 g, 2.70 mmol) in THF (35 ml), kept under an inert N_2 atmosphere, t-BuLi (2.13 ml of 1.5 M solution in pentane, 3.20 mmol) was added. After 1h, $B(OBu)_3$ (1.09 ml, 4.05 mmol) was added and the mixture was stirred for 1h to produce a boronic ester intermediate. In a separate flask 1-bromo-4-iodobenzene (1.53 g, 5.40 mmol), $Pd(PPh_3)_4$ (0.094 g, 0.081 mmol), THF (15 ml), (aq.) 2M Na_2CO_3 (10 ml) and ethylene glycol (15 drops) were preheated to 80 ^{o}C and the boronic ester solution was added slowly. The reaction mixture was heated under reflux overnight, diluted with diethyl ether (200 ml) and washed with water (200 ml). The water layer was washed with an additional volume of ether (200 ml) and the combined organic phases were dried over Na_2SO_4 and concentrated. Subsequent chromatography on silica gel (hexane) afforded compound **7** as a sticky oil (0.96 g, 72 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.00 (s, 3H), 2.01 (s, 3H), 2.06-2.11 (m, 2H), 2.81-2.87 (m, 4H), 7.01 (s, 1H), 7.03 (s, 1H), 7.23-7.25 (m, 1H) 7.31-7.36 (m, 4H), 7.43-7.51 (m, 4H) ppm. ^{13}C NMR (75.4, $CDCl_3$): δ = 14.4 (q), 23.0 (t), 38.4 (t), 38.4 (t) 120.6 (s), 123.9 (d), 124.5 (d), 125.3 (d), 126.8 (d), 127.0 (d), 128.8 (d), 131.8 (d), 134.4 (s), 134.5 (s), 134.9 (s), 135.4 (s), 136.5 (s), 136.8 (s), 137.9 (s), 139.8 (s) ppm. HRMS: calcd. for $C_{27}H_{23}S_2Br$ 490.042, found 490.041.

1-[5-(4-Acetylsulfanylphenyl)-2-methylthien-3-yl]-2-(2-methyl-5-phenylthien-3-yl)cyclopentane (2):

Compound **7** (1.3 g, 2.64 mmol) was dissolved in THF (50 ml) and the solution was cooled to -80 ^{o}C. To this solution was added dropwise t-BuLi (1.94 ml of 1.5 M solution in pentane, 2.91 mmol). After 2h S_8 (0.085 g, 2.64 mmol) dissolved in THF (4 ml) was added and the mixture was allowed to reach slowly room temperature. After 2h the reaction mixture was cooled to 0 °C and acetyl chloride (0.38 ml, 5.28 mmol) was added. After 3h the mixture was diluted with dichloromethane, washed with water and the organic phase dried (Na_2SO_4) and concentrated. Subsequent chromatography (hexane / dichloromethane 7:2) afforded compound **2** (0.67 g, 47 %) as a sticky oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.02 (s, 3H), 2.04 (s, 3H), 2.10-2.14 (m, 2H), 2.44 (s, 3H), 2.85-2.90 (m, 4H), 7.07 (s, 1H), 7.11 (s, 1H), 7.22-7.27 (m, 1H), 7.33-7.40 (m, 4H), 7.51-7.56 (m, 4H) ppm. ^{13}C NMR (75.4, $CDCl_3$): δ = 14.4 (q),14.5 (q), 23.0 (t), 30.1 (q), 38.4 (t), 38.5 (t), 123.9 (d), 124.9 (d), 125.3 (d), 125.8 (d), 125.9 (s), 126.9 (d), 128.7 (d), 134.3 (s), 134.4 (s), 134.8 (d), 134.9 (s), 135.4 (s), 135.6 (s), 136.5 (s), 136.9 (s), 138.5 (s), 139.7 (s), 194.1 (s) ppm. HRMS: calcd. for $C_{29}H_{26}OS_3$ 486.115, found 486.114.

1-(5-Chloro-2-methylthien-3-yl)-2-[5-(5-methylthien-2-yl)-2-methylthien-3-yl]cyclopentene (8):

To a solution of compound **4** (2.25 g, 6.83 mmol) in THF (100 mL), kept under an inert N_2 atmosphere, t-BuLi (4,70 mL of 1.6 M solution in hexane, 7.51 mmol) was added. After 1h, $B(OBu)_3$ (2.77 mL, 10.3 mmol) was added and the mixture was stirred for 1h to produce a boronic ester intermediate. In a separate flask 2-bromo-5-methylthiophene (1.56 mL, 13.66 mmol), $Pd(PPh_3)_4$ (0.237 g, 0.21 mmol), THF (23 mL), 2M Na_2CO_3(aq.) (18 mL) and ethylene glycol (20 drops) were preheated to 80 °C and the boronic ester solution was added slowly. The reaction mixture was heated under reflux overnight, diluted with diethyl ether (200 mL) and washed with water (200 mL). The water layer was washed with an additional volume of ether (200 mL) and the combined organic phases were dried over Na_2SO_4 and concentrated. Subsequent chromatography on silica gel (hexane) afforded compound **8** as a sticky oil (1.82 g, 68 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 1.88 (s, 3H), 1.93 (s, 3H), 1.98-2.08 (m, 2H), 2.46 (s, 3H), 2.71-2.80 (m, 4H), 6.61-6.62 (m, 2H), 6.76 (s, 1H), 6.48 (d, J=3.7 Hz, 1H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ_C 14.1 (q), 14.2 (q), 15.3 (q), 22.8 (t), 38.3 (t), 38.4 (t), 122.8 (d), 123.6 (d), 125.0 (s), 125.7 (d), 126.8 (d), 133.2 (s), 133.4 (s), 133.5 (s), 133.8 (s), 135.0 (s), 135.3 (s), 135.9 (s), 138.5 (s), ppm. HRMS: calcd. for $C_{21}H_{19}S_2Cl$ 370.062, found 370.063.

1-[2-Methyl-5-(5-methylthien-2-yl)thien-3-yl]-2-[2-methyl-5-(thien-2-yl)thien-3-yl]cyclopentene (9):

To a solution of compound **8** (1.34 g, 3.43 mmol) in THF (50 ml), kept under an inert N_2 atmosphere, t-BuLi (2.74 ml of 1.5 M solution in pentane, 4.11 mmol) was added. After 1h, $B(OBu)_3$ (1.39 ml, 5.15 mmol) was added and the mixture was stirred for 1h to produce a boronic ester intermediate. In a separate flask 2-bromothiophene (0.66 ml, 6.86 mmol), $Pd(PPh_3)_4$ (0.119 g, 0.10 mmol), THF (19 ml), (aq.) 2M Na_2CO_3 (13 ml) and ethylene glycol (18 drops) were preheated to 80 °C and the boronic ester solution was added slowly. The reaction mixture was heated under reflux overnight, diluted with diethyl ether (200 ml) and washed with water (200 ml). The water layer was washed with an additional volume of ether (200 ml) and the combined organic phases were dried over Na_2SO_4 and concentrated. Subsequent chromatography on silica gel (hexane) afforded compound **9** as a sticky oil (1.08 g, 72 %). ^{1}H NMR (300

MHz, $CDCl_3$): δ = 1.96 (s, 3H),1.97 (s, 3H), 2.05-2.10 (m, 2H), 2.47 (s, 3H), 2.82 (t, J=7.7 Hz, 4H), 6.63 (d, J=3.7 Hz, 1H), 6.82 (s, 1H), 6.85 (d, J=3.7 Hz, 1H), 6.91 (s, 1H), 6.98-7.00 (m, Hz, 1H), 7.07 (d, J=3.3 Hz, 1H), 7.16 (d, J=5.1 Hz, 1H) ppm. ^{13}C NMR (75.4, $CDCl_3$): δ = 13.8 (q), 14.9 (q), 22.5 (t), 38.0 (t), 122.3 (d), 122.4 (d), 123.1 (d), 123.2 (d), 124.0 (d), 125.3 (d), 127.1 (d), 132.5 (s), 134.9 (s), 133.0 (s), 133.5 (s), 133.9 (s), 134.1 (s), 134.9 (s), 135.7 (s), 135.9 (s), 137.3 (s), 138.0 (s) ppm. HRMS: calcd. for $C_{24}H_{22}S_4$ 438.060, found 438.062.

1-[5-(5-Acetylsulfanylthien-2-yl)-2-methylthien-3-yl]-2-[2-methyl-5-(5-methylthien-2-yl)thien-3-yl]cyclopentene (3):

Compound **9** (1 g, 2.28 mmol) was dissolved in THF (50 ml) and the solution was cooled to -80 °C. To this solution was added dropwise t-BuLi (1.82 ml of 1.5 M solution in pentane, 2.74 mmol). After 2h S_8 (0.073 g, 2.28 mmol) dissolved in THF (4 ml) was added and the mixture was allowed to reach slowly room temperature. After 2h the reaction mixture was cooled to 0 °C and acetyl chloride (0.32 ml, 4.56 mmol) was added. After 3h the mixture was diluted with dichloromethane, washed with water and the organic phase dried (Na_2SO_4) and concentrated. Subsequent chromatography (hexane / dichloromethane 7:2) afforded compound **3** (0.67 g, 57 %) as a sticky oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.95 (s, 3H), 1.97 (s, 3H), 2.07-2.10 (m, 2H), 2.42 (s, 3H), 2.47 (s, 3H), 2.81 (t, *J*=7.3 Hz, 4H), 6.63 (d, J=3.3 Hz, 1H), 6.81 (s, 1H), 6.85 (d, J=3.3 Hz, 5H), 6.93 (s, 1H), 7.03 (s, 2H) ppm. ^{13}C NMR (75.4, $CDCl_3$): δ = 14.2 (q), 14.3 (q), 15.3 (q), 22.9 (t), 29.4 (q), 38.4 (t), 122.7 (s), 122.8 (d), 123.2 (d), 123.7 (d), 125.3 (d), 125.7 (d), 132.1 (s), 133.3 (s), 133.5 (s), 134.1 (s), 134.9 (s), 135.0 (s), 135.3 (s), 136.0 (s), 136.5 (s), 136.6 (d), 138.4 (s), 144.1 (s), 194.3 (s) ppm. HRMS: calcd. for $C_{26}H_{24}OS_5$ 512.125, found 512.124.

Preparation of gold nanoparticles:

A typical synthetic procedure is as follows: The $HAuCl_4$ (135 mg, 0.343 mmol) in water (34 ml) was added to tetraoctylammonium bromide (375 mg, 0.686 mmol) in toluene (92 ml), and the mixture was vigorously stirred. The yellow aqueous solution became colorless, and the toluene phase turned orange. After 10 min, freshly deprotected [with NH_4OH (0.84 ml of 25 % aq. solution) in THF (16 ml) stirred for 30 min and evaporated] **1o** (167 mg, 0.343 mmol) in toluene (12 ml) was added and mixture was stirred for 10 min. A freshly prepared solution of $NaBH_4$ (129 mg, 3.34 mmol) in water (34 ml) was added to the vigorously stirred solution. The resulting mixture continued to be stirred overnight. The organic phase was then separated, evaporated and dried in vacuum for a day. The crude solid was dissolved in toluene (15 ml) and mixed with methanol (150 ml). The dark precipitate was filtered of and washed with methanol. Size-exclusion chromatography (sephadex LH-20, 1 m column in THF) gives **Au-1o** separated from remaining thiol and tetraoctylammonium bromide.

Transmission Electron Microscopy (TEM)

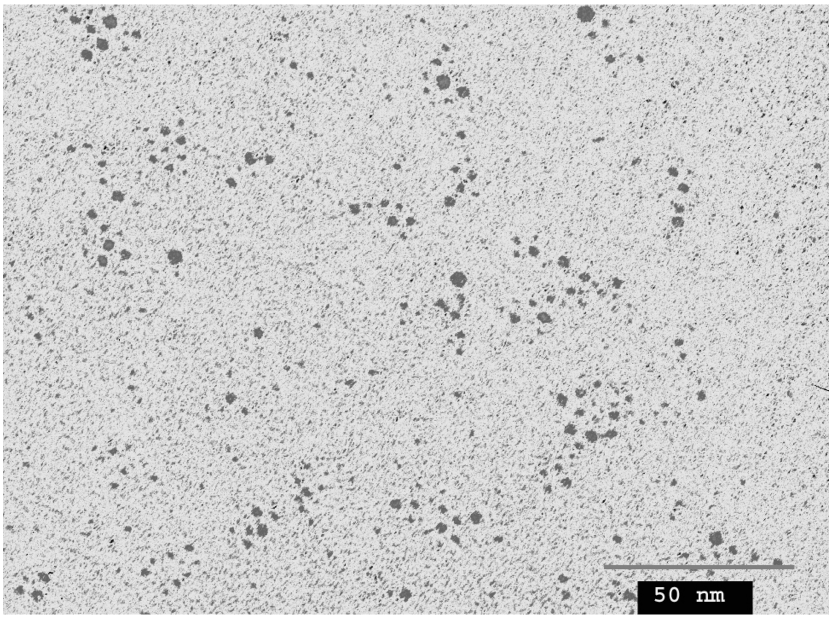


Fig. 1. Representative TEM image of **Au-1o**, deposited on a carbon-coated Cu-grid film by drop-casting from a dilute toluene solution. An average size of gold nanoparticles is 2.0 nm.

UV/Vis Measurements

UV/Vis measurements were performed on a Hewlett-Packard HP 8453 diode array spectrophotometer. Stock solutions were prepared using Uvasol grade toluene and were stored in the dark. Irradiations were performed with a high pressure mercury/xenon lamp (200W, Oriel) and appropriate highpass or bandpass filters (Andover corporation)

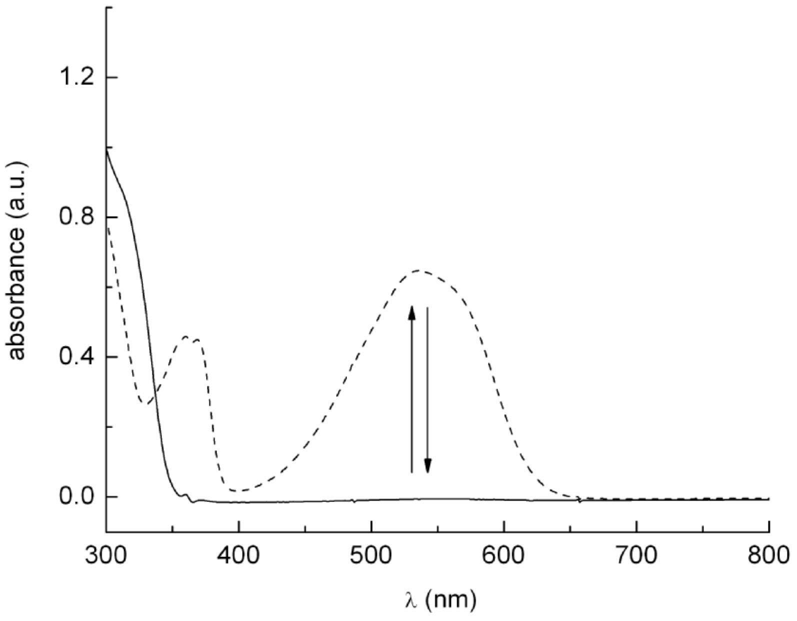


Fig.2 UV/Vis spectra of **1** open form (—) and closed form (---) in toluene.

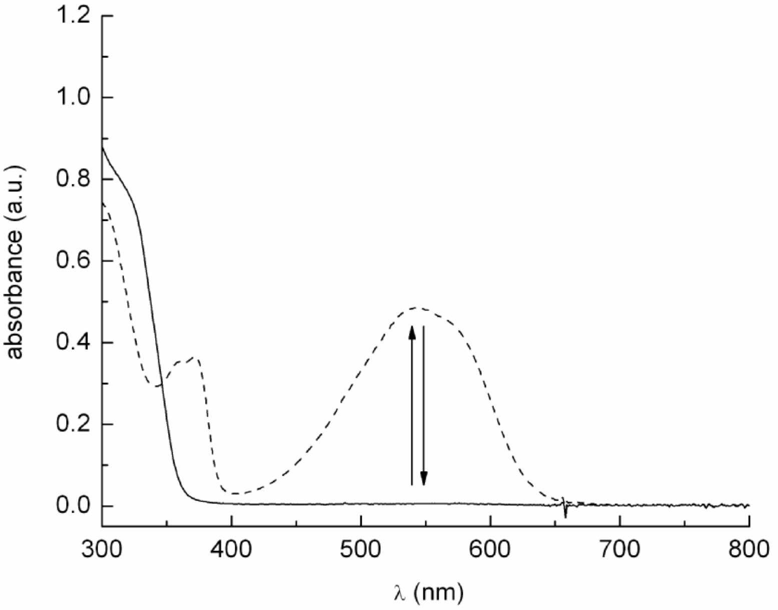


Fig.3 UV/Vis spectra of **2** open form (—) and closed form (---) in toluene.

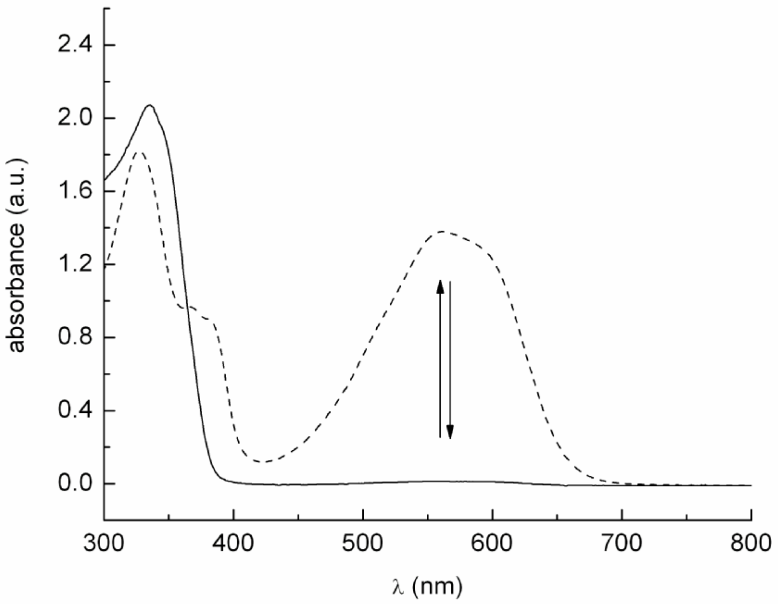


Fig.4 UV/Vis spectra of **3** open form (—) and closed form (---) in toluene.

Reflectance FT-IR spectra:

The IR spectroscopy measurements were performed on a Nicolet Nexus FT-IR apparatus. Solid diarylethenes or diarylethene-modified gold nanoparticles were grinded together with the KBr and the final powder was equally spread on the sample holder.

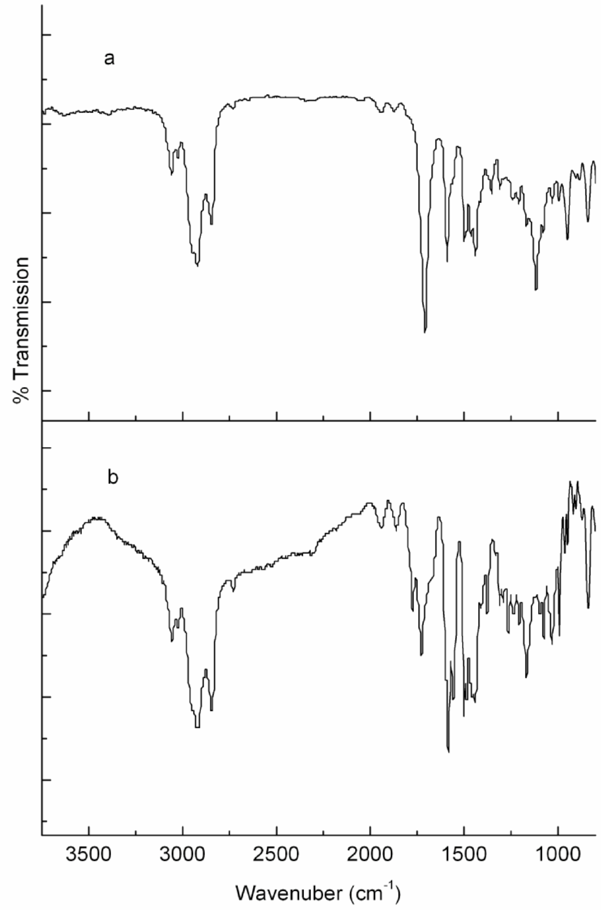


Fig. 5 FT-IR spectra of **1o** (a) and **Au-1o** (b).

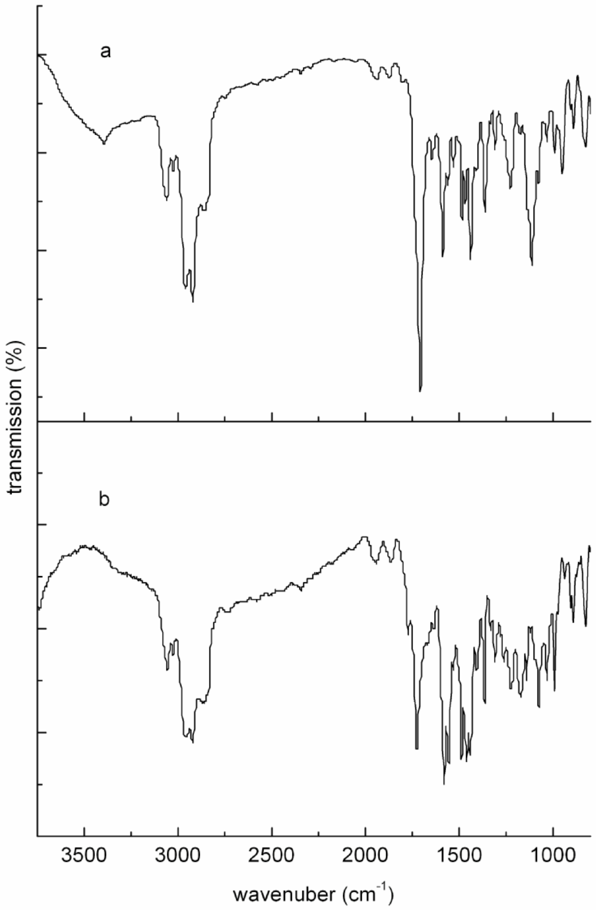


Fig. 6 FT-IR spectra of **1c** (a) and **Au-1c** (b).

References

[1] L. N. Lucas, J. van Esch, R. M. Kellogg and B. L. Feringa, *Chem. Commun.*, 1998, 2313-2314.