Electronic Supplementary Information

Sequential self-assembly for construction of Pt(II)-bridged [3]rotaxanes on gold nanoparticles

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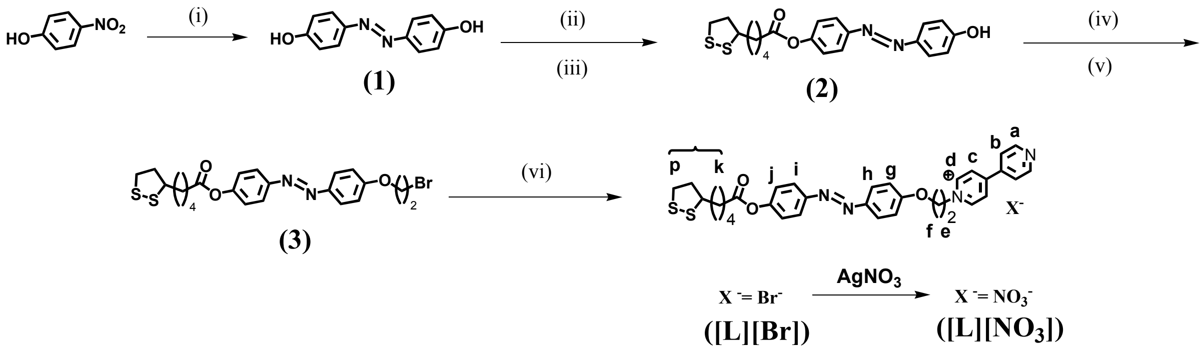
General. ^{1}H NMR, ^{13}C NMR, and ^{1}H NOESY NMR spectra were recorded on either a Bruker AV 400 or a BBFO 400 spectrometer. The electronic spray ionization (ESI) mass spectra were recorded on either a HP5989 mass spectrometer or a ThermoFinnigan LCQ quadrupole ion trap mass spectrometer. Melting points were determined by using an X-6 micro-melting point apparatus. TEM images were collected from an FEI EM 208S TEM (Philips) operated at 100 kV. Raman spectra were recorded from the sample solution in a cuvette (path length = 1.00 cm) on an R-3000HR spectrometer with a red light-emitting diode (LED) laser source (λ = 785 nm) at 290 mW. Absorption spectra were recorded on a Shimadzu UV-3600 UV-Vis-NIR spectrophotometer (1 mm quartz cell was used), and the ICD spectra were recorded on a Jasco J-810 CD spectrophotometer using a 1 cm quartz cell. The photoirradiation was carried out on a LE-EM 500 Xenon lamp with a filter for 365 nm. The distance between the lamp and the sample cuvette is about 20 cm. The vial images were photographed by a Nikon COOLPIX S8000 digital camera. Elemental analysis was performed on a EuroVector Euro EA Elemental Analyzer.

Materials. α-cyclodextrin (α-CD), 4-nitrophenol, 1,2-dibromoethane, (±)-α-lipoic acid, 4,4'-bipyridine, dicyclohexyl carbodiimide (DCC), 4-dimethylamino pyridine (DMAP), sodium citrate, silver nitrate, and hydrogen tetrachloroaurate were purchased from Alfa Aesar and used as received. Ethylene diamine palladium chloride and ethylene diamine platinum chloride were purchased from Sigma-Aldrich and used as received. Acetone was dried with anhydrous magnesium sulfate before uses. THF was refluxed over sodium particles and distilled before uses. The vials, stirring bars, and cuvettes were pretreated with aqua regia before uses.



Scheme S1. Synthetic route for preparation of the ligand [L][NO_3]. Reagents and conditions: (i) potassium hydroxide, (ii) (±)-α-lipoic acid, (iii) DMAP and DCC, (iv) 1,2-dibromoethane, (v) potassium carbonate, and (vi) 4,4'-bipyridine. The protons are defined alongside the structural formula.

1: This compound was synthesized based on previous method that have reported,[S1] but with some slight modifications. In short, 4-nitrophenol (15.6 g, 0.11 mol), KOH (80 g, 1.43 mol), and deionized H_2O (16 mL) were mixed together and heated to 200 °C by a heating mantle with manual stirring. H_2O was evaporated during the reaction. After the mixture was stirred for 1 h, it was cooled down to room temperature and then acidified with hydrochloric acid. The precipitates formed were filtered and washed with H_2O. Pure compound **1** (7.8 g, 65%) as a yellow solid was obtained by recrystallization from ethanol/water (1:3). m.p. 212–214 °C.

2: A mixture of (±)-*α*-lipoic acid (2.0 g, 9.7 mmol), **1** (2.1 g, 9.8 mmol), DCC (2.0 g, 9.7 mmol), and DMAP (59 mg, 0.5 mmol) in anhydrous THF (80 mL) was stirred at 60°C for 24 h. The solvent was removed in vacuo, and the residue was recrystallized twice with industrial alcohol to give yellow compound **2** (2.53 g, 64.9%). m.p. 128 ~ 129 ºC. ^{1}H NMR (400 MHz, $CDCl_3$, 298K, TMS): $\delta = 7.93$ (d, $J = 8.8$ Hz, 2H), 7.89 (d, $J = 8.4$ Hz, 2H), 7.24 (d, $J = 8.8$ Hz, 2H), 6.96 (d, $J = 8.8$ Hz, 2H), 5.22 (s, 1H), 3.65 (m, 1H), 3.22 (m, 1H), 3.15 (m, 2H), 2.64 (t, $J = 7.2$ Hz, 2H), 2.50 (m, 1H), 1.90 (m, 1H), 1.82 (m, 2H), 1.60 (m, 2H), 1.29 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, 298K, TMS): $\delta = 172.31$, 158.69, 152.03, 150.42, 146.87, 124.98, 123.78, 122.15, 115.81, 56.32, 40.27, 38.54, 34.61, 34.24, 28.72, 24.62. HRMS (ESI): calcd for $C_{20}H_{21}N_2O_3S_2$ m/z = 401.0994, found m/z = 401.0997 [**2** − H]$^-$. Elemental analysis: calcd C 59.68, H 5.51, N 6.96; found C 59.31, H 5.94, N 6.62.

3: Compound **2** (0.5 g, 1.24 mmol) was added to an acetone solution (12 mL) containing 1,2-dibromoethane (2.4 g, 12.9 mmol). The mixture solution was then added K_2CO_3 (355 mg, 2.57 mmol). The solution was stirred under refluxing for 8 h under Ar protection. After filtration, the filtrate was concentrated *in vacuo* and then purified through silica gel chromatography (petroleum ether : ethyl acetate = 9 : 2) to afford yellow compound **3** (0.395 g, 62.7%). m.p. 107 ~ 108 ºC. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, TMS): δ = 7.97 (d, *J* = 8.8 Hz, 2H), 7.90 (d, *J* = 8.8 Hz, 2H), 7.25 (d, *J* = 8.8 Hz, 2H), 7.04 (d, *J* = 8.8 Hz, 2H), 4.40 (t, *J* = 6.0 Hz, 2H), 3.71 (t, *J* = 6.0 Hz, 2H), 3.65 (m, 1H), 3.22 (m, 1H), 3.16 (m, 1H), 2.64 (t, *J* = 7.2 Hz, 2H), 2.50 (m, 1H), 1.90 (m, 1H), 1.80 (m, 2H), 1.60 (m, 2H), 1.29 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, 298K, TMS): δ = 171.69, 152.73, 152.29, 150.14, 147.34, 124.83, 124.10, 122.23, 114.94, 68.04, 56.31, 40.26, 38.54, 34.62, 34.20, 28.81, 28.73, 24.61. HRMS (ESI): calcd for $C_{22}H_{26}N_2O_3S_2Br$ m/z = 509.0568, found m/z = 509.0565 (^{79}Br), 511.0553 (^{81}Br) [**3** + H]$^+$.

[L][NO$_3$]: An acetonitrile solution (20 mL) containing **3** (0.36 g, 0.71 mmol) and 4,4'-bipyridine (1.1 g, 7.09 mmol) was stirred at 80°C for 2 d. The solvent was removed *in vacuo*. The residue was dissolved in a small amount of acetonitrile and then purified through silica gel chromatography (dichloromethane : methanol = 50 : 5) to afford white compound [L][Br] (0.33 g, 70.2%). m.p. >250 ºC. ^{1}H NMR (400 MHz, $CDCl_3$, 298K, TMS): δ = 9.73 (d, *J* = 5.6 Hz, 2H), 8.85 (d, *J* = 5.2 Hz, 2H), 8.20 (d, *J* = 6.0 Hz, 2H), 7.83 (d, *J* = 8.4 Hz, 2H), 7.80 (d, *J* = 8.0 Hz, 2H), 7.57 (d, *J* = 5.6 Hz, 2H), 7.15 (d, *J* = 8.4 Hz, 2H), 6.93 (d, *J* = 8.8 Hz, 2H), 5.60 (m, 2H), 4.69 (m, 2H), 3.55 (m, 1H), 3.10 (m, 2H), 3.16 (m, 2H), 2.54 (t, *J* = 7.6 Hz, 2H), 2.41 (m, 1H), 1.88 (m, 1H), 1.74 (m, 2H), 1.54 (m, 2H), 1.25 (m, 2H). ^{13}C NMR (100 MHz, DMSO-d_6, 298K, TMS): δ = 171.53, 160.12, 152.80, 152.29, 150.97, 149.51, 146.55, 146.01, 140.78, 125.22, 124.56, 123.47, 122.84, 121.94, 115.33, 66.46, 59.39, 56.01, 38.11, 34.00, 33.28, 27.99, 24.00. HRMS (ESI): calcd for $C_{32}H_{33}N_4O_3S_2$ m/z = 585.1994, found m/z: 585.2042 $[\mathbf{M} - Br]^+$. Elemental analysis: calcd C 57.74, H 5.00, N 8.42; found C 57.72, H 5.35, N 9.50.

$AgNO_3$ (47 mg, 0.28 mmol) was then added to a water solution (20 mL) containing [L][Br] (180 mg, 0.27 mmol) and the mixture solution was stirred at 45 °C in dark for 8 h. The solid formed was collected by filtration and the product was extracted with acetone (30 mL). After removing solvent and drying under reduced pressure, pure $[L][NO_3]$ was obtained as a yellow solid (138 mg, 78.8%). Its proton resonances are almost the same as those of [L][Br].

enPt: Ethylene diamine platinum chloride (60 mg, 0.18 mmol) was suspended in H_2O (20 mL) at 50 °C. $AgNO_3$ (64 mg, 0.38 mmol) was added to the suspension and the mixture solution was stirred for 2 h. White AgCl solid was formed and then filtered off. The filtrate was evaporated *in vacuo* and the white solid product was directly used for the next step.

Citrate-Stabilized AuNPs with an Average Diameter of 15 nm: It was prepared by following the synthetic procedure described in literature.[S2]

Au@[L(α-CD)][NO$_3$] and Au@[Pt-2L(α-CD)$_2$][NO$_3$]$_4$: Two of the hybrids were prepared by the ligand-exchange reaction. Typically, $[L(\alpha\text{-CD})][NO_3]$ or $[Pt\text{-}2L(\alpha\text{-CD})_2][NO_3]_4$ aqueous solution (1 mL, 10 mM calculated by the azobenzene unit) was placed in a 4-mL cleaned vial. Citrate-stabilized AuNP solution (2 mL, 14.25 nM calculated by the gold spheres) was dropwise added to the ligand solution with stirring. $Au@[L(\alpha\text{-CD})][NO_3]$ was formed immediately and deposited as black precipitates, whereas $Au@[Pt\text{-}2L(\alpha\text{-CD})_2][NO_3]_4$ was generated stably and isolated by centrifugation.

Job Plot of Complexation between [L][NO$_3$] and α-CD

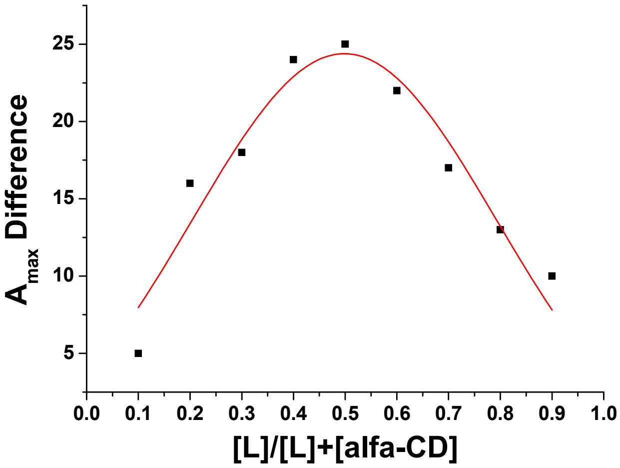


Fig. S1 Job plot showing 1:1 stoichiometry of the host-guest complex between [L][NO$_3$] and α-CD in H_2O. The total concentration of the host and guest was kept at 1.0×10^{-4} M.

Association Constant *k* between [L][NO$_3$] and α-CD

The association constant *k* between [L][NO$_3$] and α-CD in aqueous solution was determined by following the UV-Vis absorption changes at 440 nm as shown in Fig. S2. The concentration of [L][NO$_3$] maintains unchanged at 1.0 × 10^{-4} M. Upon addition of α-CD, the absorption at 440 nm changes remarkably. With a 1:1 stoichiometry, the inclusion complexation between α-CD and [L][NO$_3$] is expressed by the following equation:

$$[\mathrm{L}] \quad + \quad [\alpha\text{-CD}] \quad \overset{\mathrm{K}}{\rightleftharpoons} \quad [\mathrm{L\text{-}CD}]$$

We employed the double reciprocal plot in calculation of the association constant *k* according to the modified Hidebrand-Benesi equation:[S3]

$$\frac{1}{[\Delta A]} = \frac{1}{\mathrm{K}\,[\Delta\varepsilon][\mathrm{L}]\,[\alpha\text{-CD}]} + \frac{1}{[\Delta\varepsilon][\mathrm{L}]}$$

where ΔA denotes the absorbance difference before and after addition of α-CD and $\Delta\varepsilon$ denotes the difference of the molar extinction coefficient between the ligand and the complex at the same wavelength.

The association constant *k* is calculated from the double reciprocal plot of $1/\Delta A$ versus 1/[α-CD], and the value calculated is 1830 ± 95 M^{-1} for the host-guest complex.

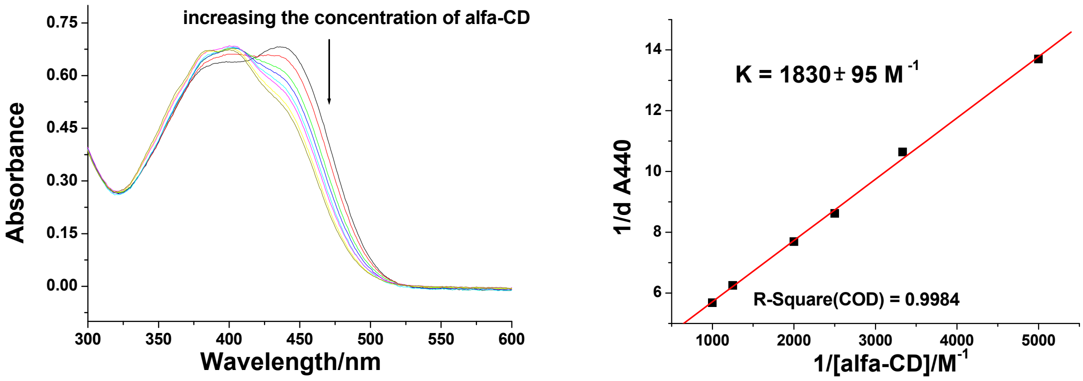


Fig. S2 UV-Vis absorption changes (left) and double reciprocal plot (right) of [L][NO_3] upon stepwise addition of α-CD. The concentration of [L][NO_3] maintains 1.0×10^{-4} M.

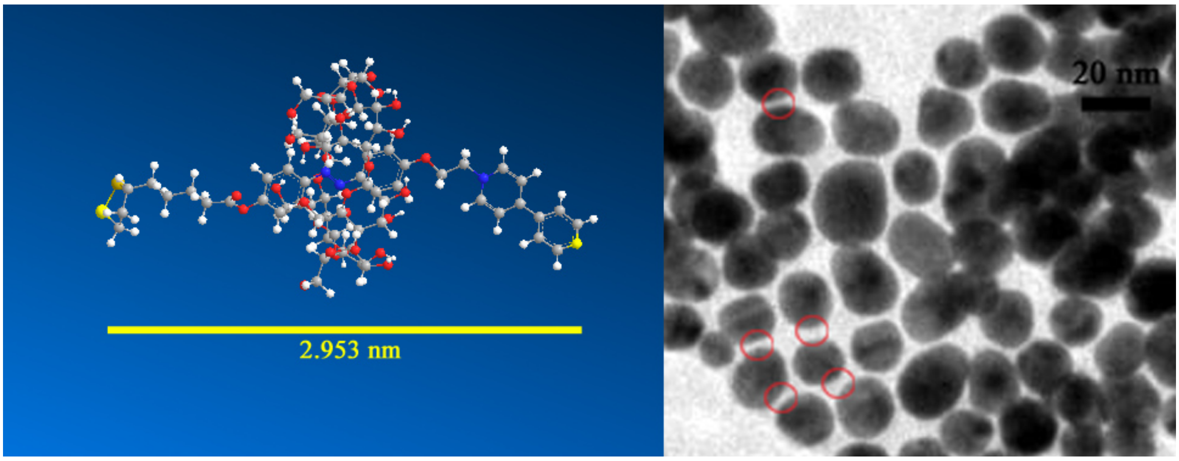


Fig. S3 Energy-minimized structure of L(α-CD)][NO_3] (left) and TEM image of Au@L(α-CD)][NO_3] (right). The distance between some of two adjacent nanoparticles has been highlighted by red ellipse, which is consistent with the length of L(α-CD)][NO_3].

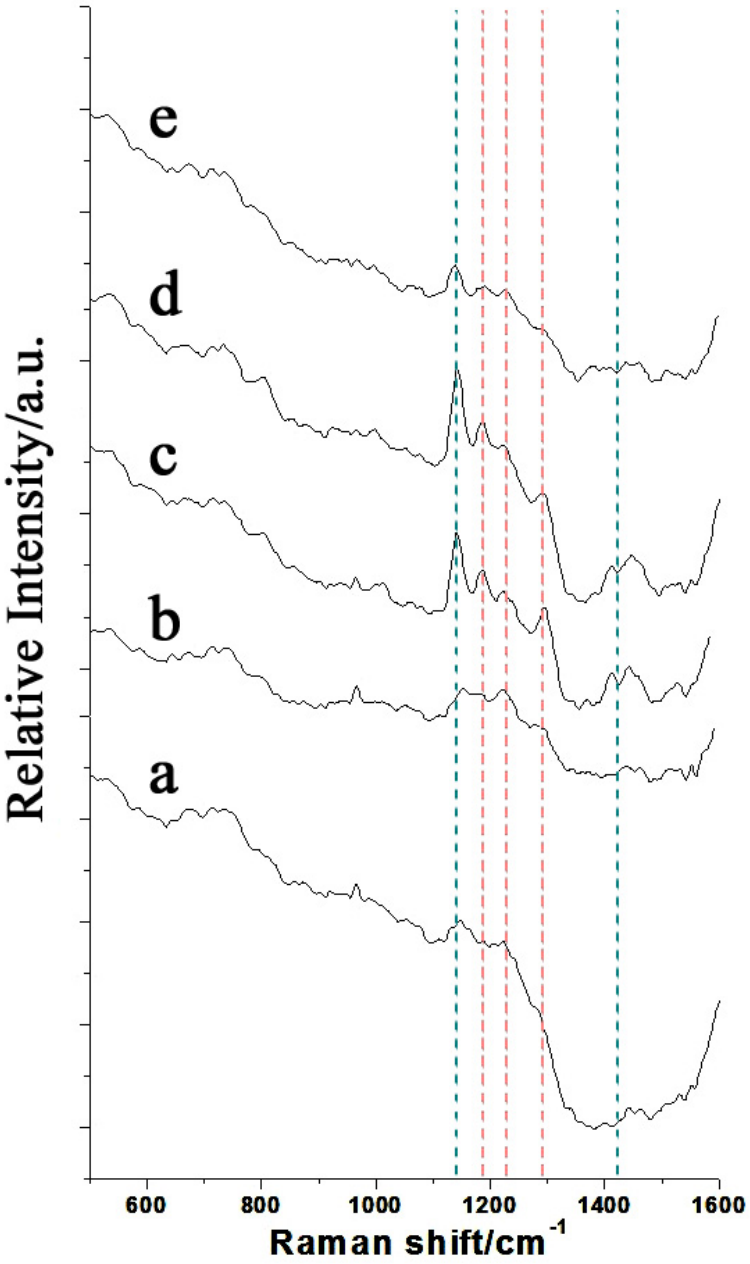


Fig. S4 Raman spectra of [L(α-CD)][NO_3] in H_2O recorded immediately by mixed with (a) H_2O, (b) enPt, (c) AuNPs, (d) AuNPs followed by enPt, and (e) enPt followed by AuNPs. The concentrations of [L(α-CD)][NO_3] and AuNPs maintaine 3.3 mM and 4.75 nM, respectively. The amount of enPt was adjusted to be half equiv of [L(α-CD)][NO_3]. The green and red dash lines denote the vibrations of azobenzene and aromatic units, respectively.[S4]

^{1}H NMR Titration Experiments

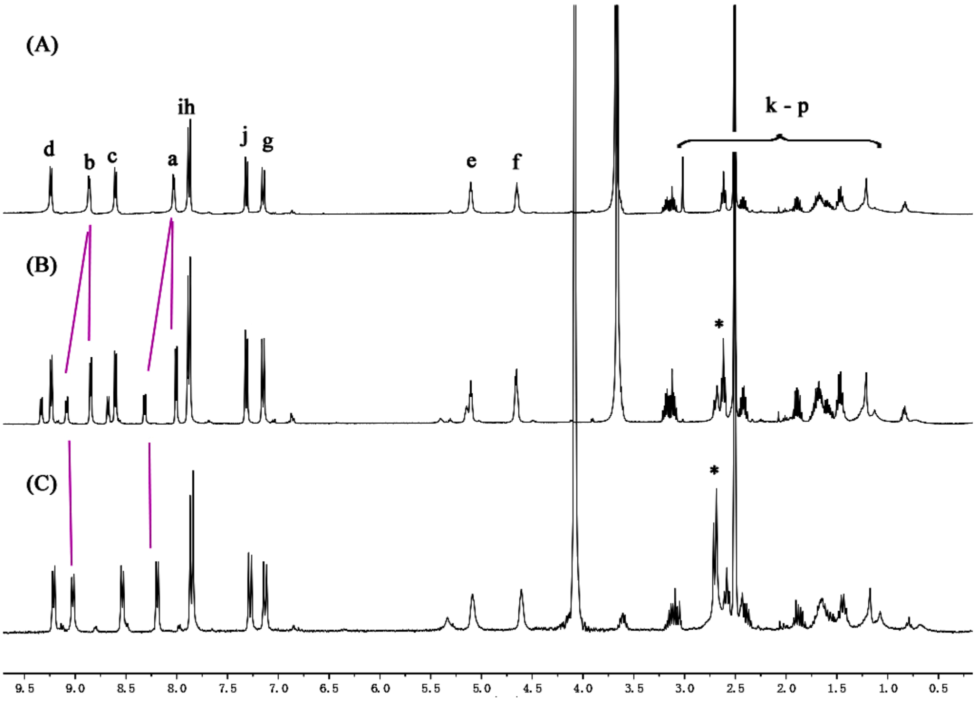


Fig. S5 ^{1}H NMR spectra (400 MHz) of (A) [L][NO_3], (B) [L][NO_3] + 0.15 equiv of enPt, and (C) [L][NO_3] + 0.5 equiv of enPt in DMSO-d_6 at 298 K. The "*" stands for the methylene protons of the coordinated ethylene diamine group.

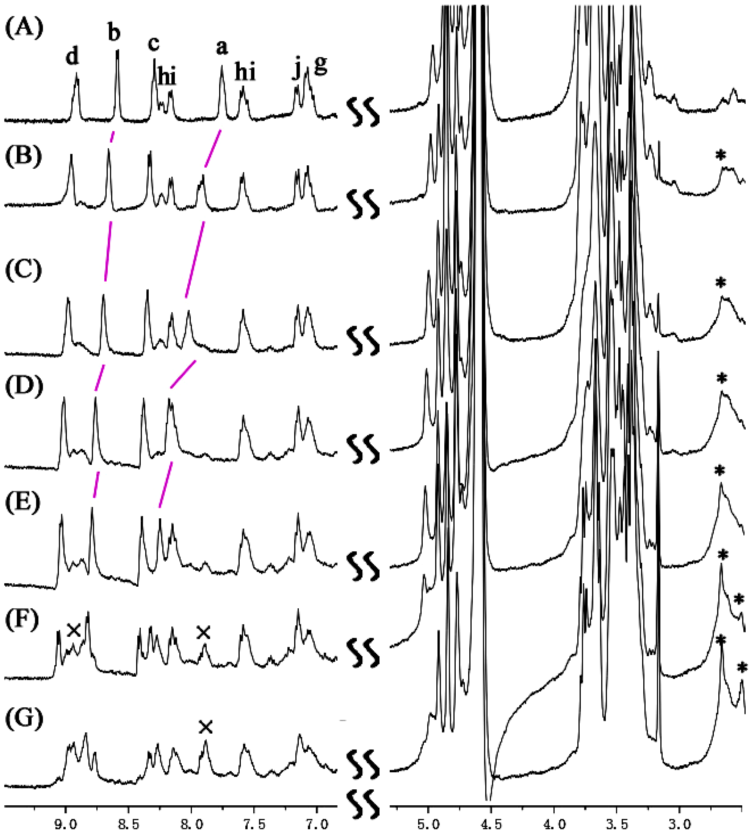


Fig. S6 ^{1}H NMR spectra (400 MHz) of (A) [L(α-CD)][NO_3], (B) [L(α-CD)][NO_3] + 0.05 equiv of enPt, (C) [L(α-CD)][NO_3] + 0.15 equiv of enPt, (D) [L(α-CD)][NO_3] + 0.35 equiv of enPt, (E) [L(α-CD)][NO_3] + 0.5 equiv of enPt, (F) [L(α-CD)][NO_3] + 0.7 equiv of enPt, and (G) [L(α-CD)][NO_3] + 1.0 equiv of enPt in D_2O at 298 K. Some impurity peaks marked with "X" emerged when more than 0.5 equiv of enPt was added, indicating that 0.5 equiv of enPt is sufficient for the quantitative formation of [Pt-2L(α-CD)$_2$][NO_3]$_4$. The "*" stands for the methylene protons of the coordinated ethylene diamine group.

^{1}H NOESY NMR Spectra

The NOE cross peaks between the azobenzene protons $H_{g\text{-}j}$ and the internal protons $H_{3/5}$ of α-CD are found in the ^{1}H NOESY NMR spectra (Fig. S7 and S8), indicating the α-CD ring dominantly encircles the azobenzene unit both in [L(α-CD)][NO_3] and [Pt-2L(α-CD)$_2$][NO_3]$_4$.

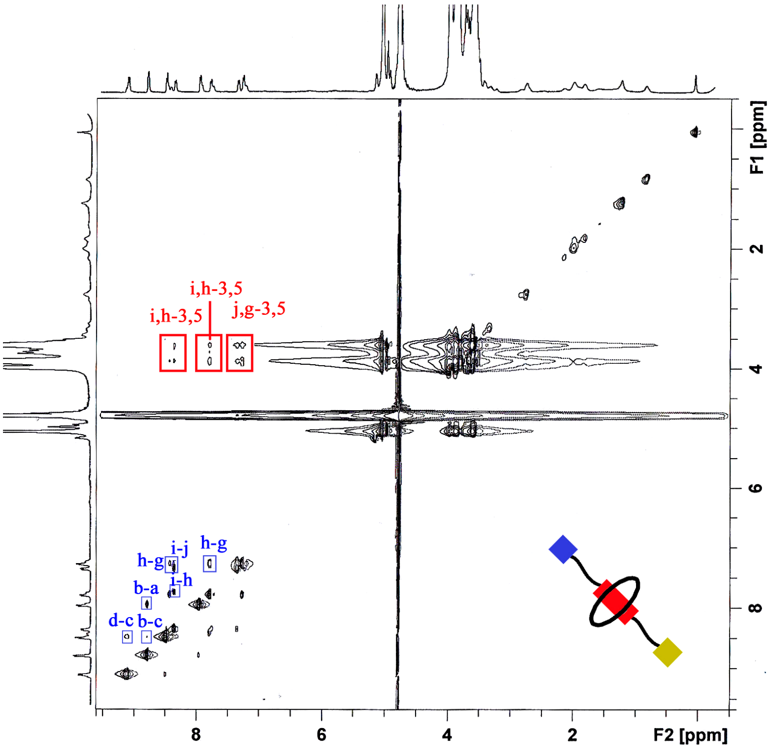


Fig. S7 ^{1}H NOESY NMR spectrum (400 MHz) of [L(α-CD)][NO_3] in D_2O at 298 K.

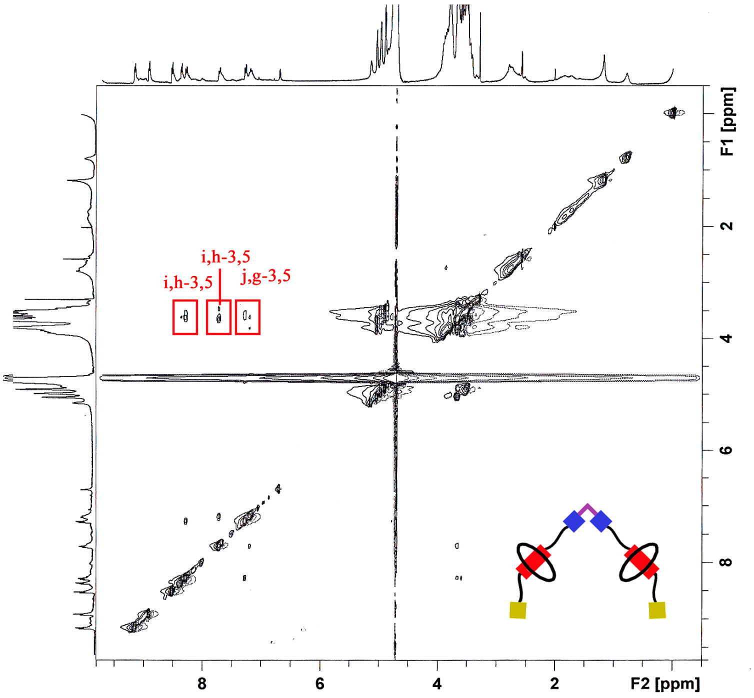


Fig. S8 ^{1}H NOESY NMR spectrum (400 MHz) of [Pt-2L(α-CD)$_2$][NO_3]$_4$ in D_2O at 298 K.

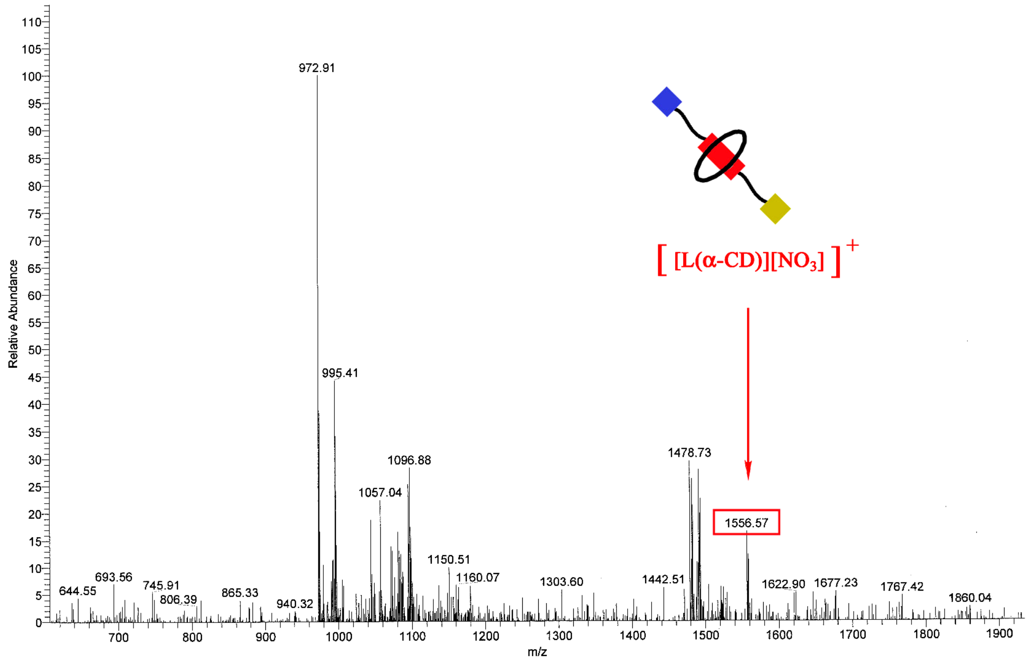


Fig. S9 ESI-MS spectrum of $[L(\alpha\text{-CD})][NO_3]$ in H_2O.

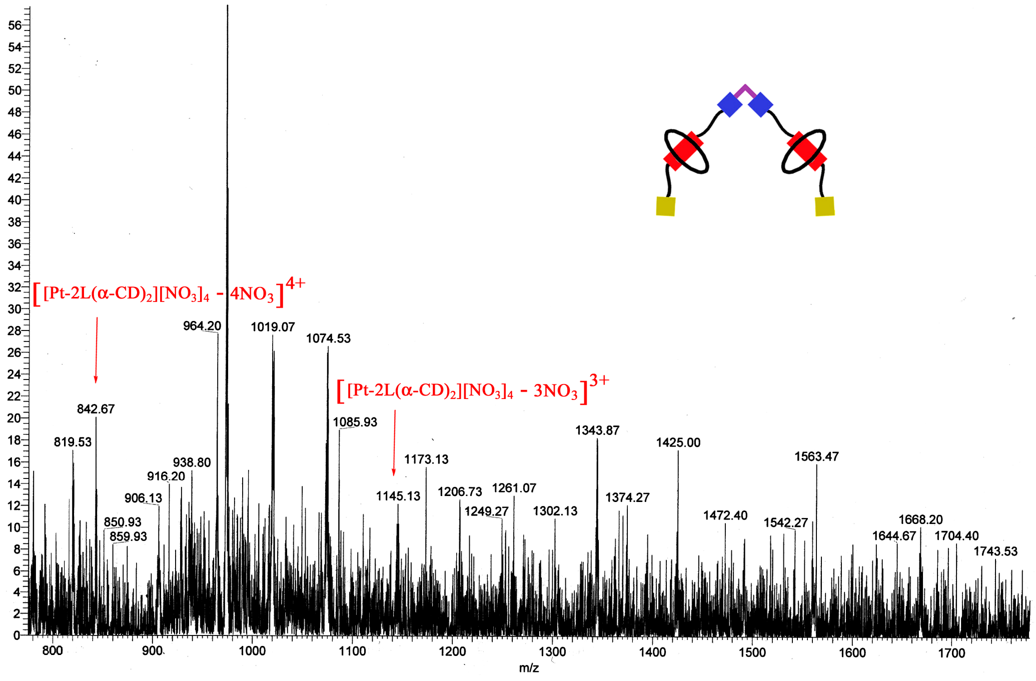


Fig. S10 ESI-MS spectrum of $[Pt\text{-}2L(\alpha\text{-CD})_2][NO_3]_4$ in H_2O.

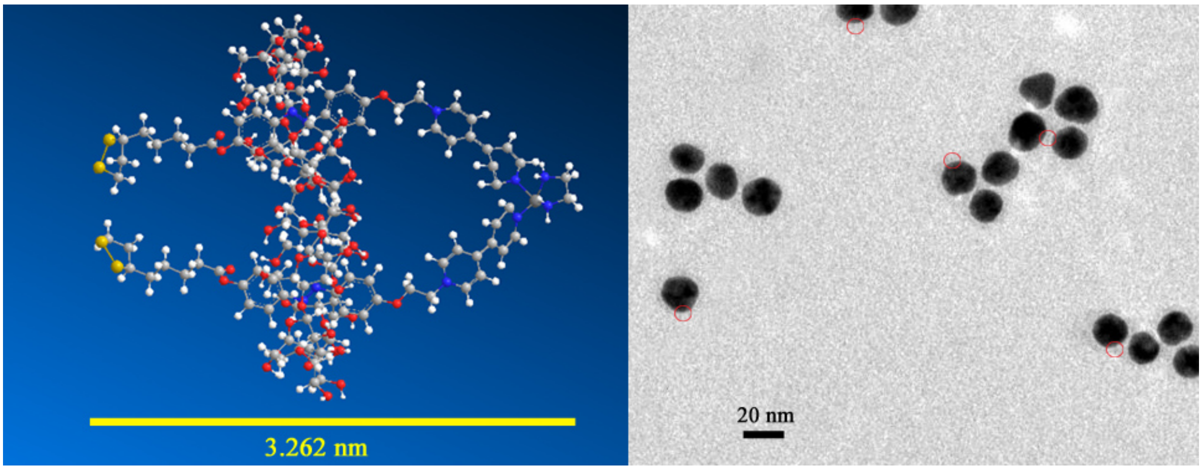


Fig. S11 Energy-minimized structure of $[Pt\text{-}2L(\alpha\text{-}CD)_2][NO_3]_4$ (left) and TEM image of $Au@[Pt\text{-}2L(\alpha\text{-}CD)_2][NO_3]_4$ (right). The ellipses highlight the thickness of the outer layer around a nanoparticle, which is consistent with the height of $L(\alpha\text{-}CD)][NO_3]$.

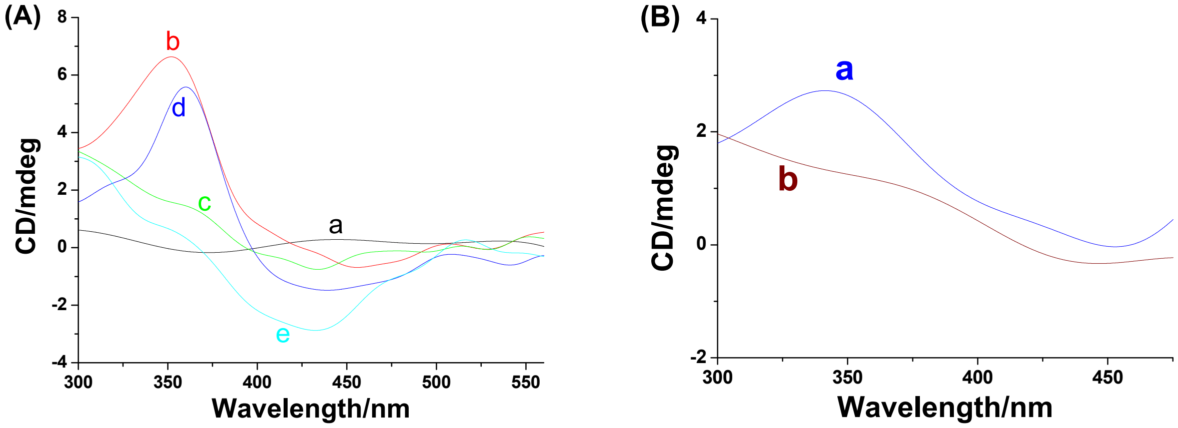


Fig. S12 (A) Induced circular dichroism (ICD) spectra of $[L][NO_3]$ (curve a), $L(\alpha\text{-}CD)][NO_3]$ (curve b), $L(\alpha\text{-}CD)][NO_3]$ irradiated by 365 nm of UV light for 20 min (curve c), $[Pt\text{-}2L(\alpha\text{-}CD)_2][NO_3]_4$ (curve d), and $[Pt\text{-}2L(\alpha\text{-}CD)_2][NO_3]_4$ irradiated by 365 nm of UV light for 20 min (curve e) in H_2O at 298 K. (B) Induced circular dichroism (ICD) spectra of $Au@[Pt\text{-}2L(\alpha\text{-}CD)_2][NO_3]_4$ (curve a) and $Au@[Pt\text{-}2L(\alpha\text{-}CD)_2][NO_3]_4$ irradiated by 365 nm of UV light for 20 min (curve b) in H_2O at 298 K.

Calculation of Coverage of $[Pt\text{-}2L(\alpha\text{-}CD)_2][NO_3]_4$ on AuNPs

The coverage of $[Pt\text{-}2L(\alpha\text{-}CD)_2][NO_3]_4$ on AuNPs was determined by UV-Vis spectroscopy and calculated from Lambert–Beer law. The initial solution of $[Pt\text{-}2L(\alpha\text{-}CD)_2][NO_3]_4$ (the concentration is 10.0 mM calculated by the azobenzene unit) was diluted 60-fold with deionized water, and used for measurement of the UV-Vis absorbance. The absorbance A_1 at 350 nm, attributed to the electronic transition π–π* of the azobenzene unit, is 2.029. A aqueous solution (2 mL) of AuNPs (14.25 nM) was added into the initial aqueous solution (1 mL) of $[Pt\text{-}2L(\alpha\text{-}CD)_2][NO_3]_4$ (10.0 mM) and stirred for 1 h. The excess AuNPs were thoroughly removed by centrifugation (13500 rpm for 15 min). The absorbance A_2 at 350 nm for the rest solution after diluted 60-fold with deionized water is 0.676. The relationship between the absorbance and the ligand concentration is reflected as the following equation:

$$A_1/A_2 = \frac{C_{\text{initial}}/60}{C_{\text{end}}/60}$$

(both the molar extinction coefficient ε and the cuvette length d are constant)

According to the result (C_{end} = 3.331 mM), we can deduce that the ligand amount consumed by these AuNPs is 5.985×10^{-9} mol. As one $[Pt\text{-}2L(\alpha\text{-}CD)_2][NO_3]_4$ molecule has two azobenzene units, the average molar ratio of $[Pt\text{-}2L(\alpha\text{-}CD)_2][NO_3]_4$ to AuNPs is 210:1.

^{1}H NMR Spectra for Compounds 2, 3 and [L][Br]

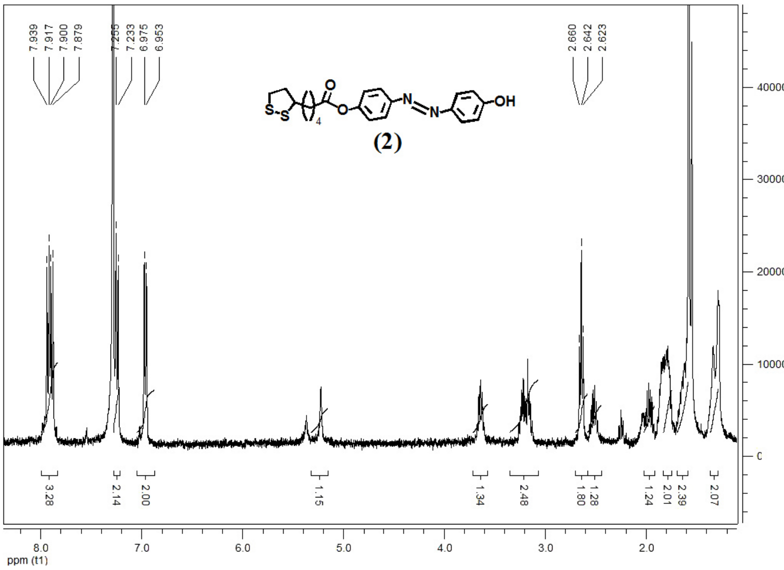


Fig. S13 ^{1}H NMR spectrum of the compound **2**.

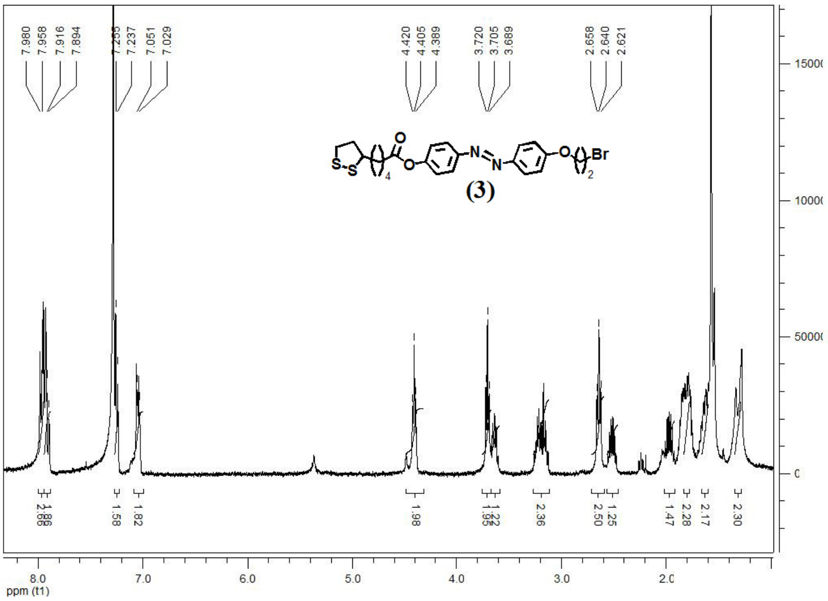


Fig. S14 ^{1}H NMR spectrum of the compound **3**.

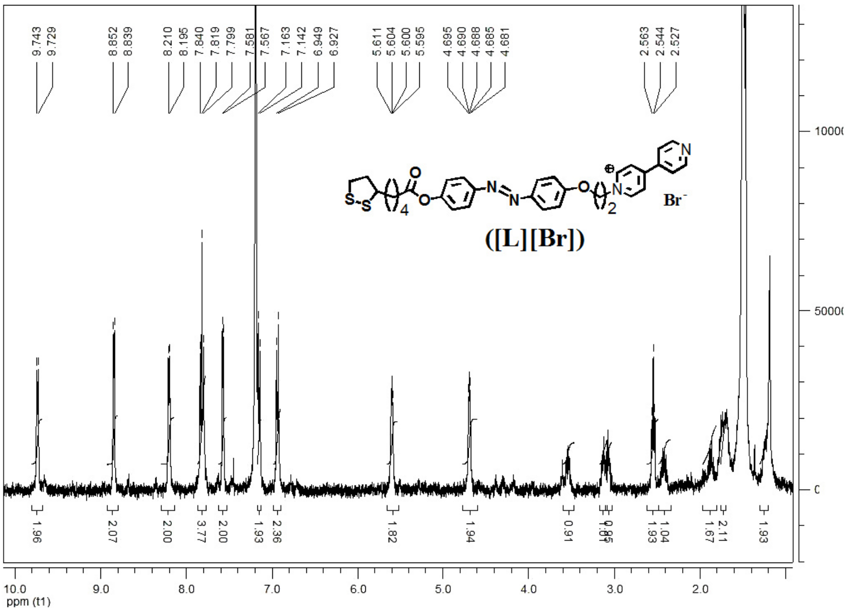


Fig. S15 ^{1}H NMR spectrum of the compound [L][Br].

^{13}C NMR Spectra for Compounds 2, 3 and [L][Br]

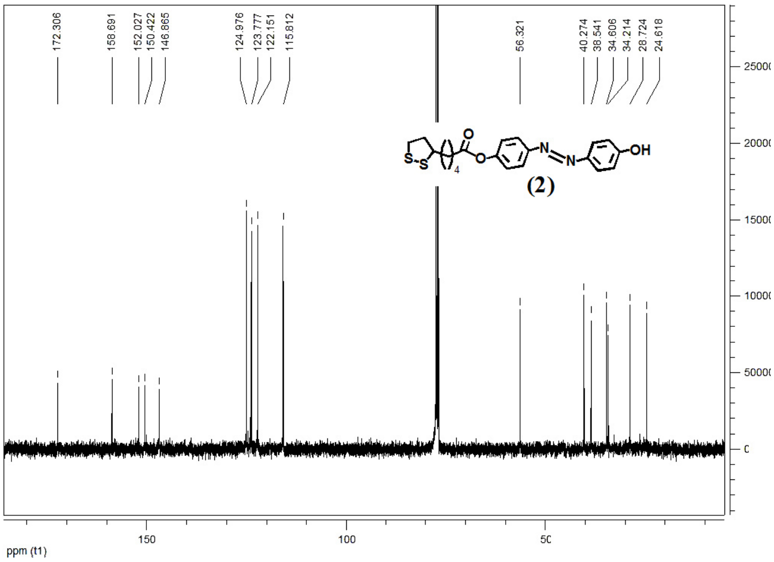


Fig. S16 ^{13}C NMR spectrum of the compound **2**.

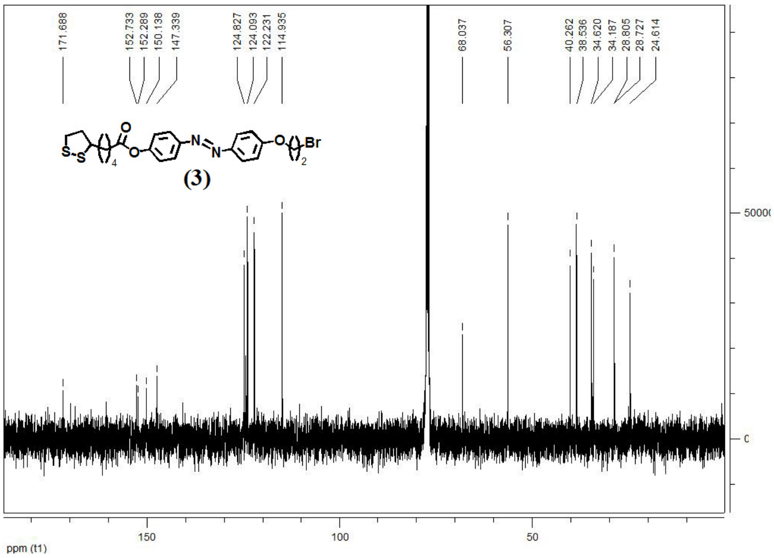


Fig. S17 ^{13}C NMR spectrum of the compound **3**.

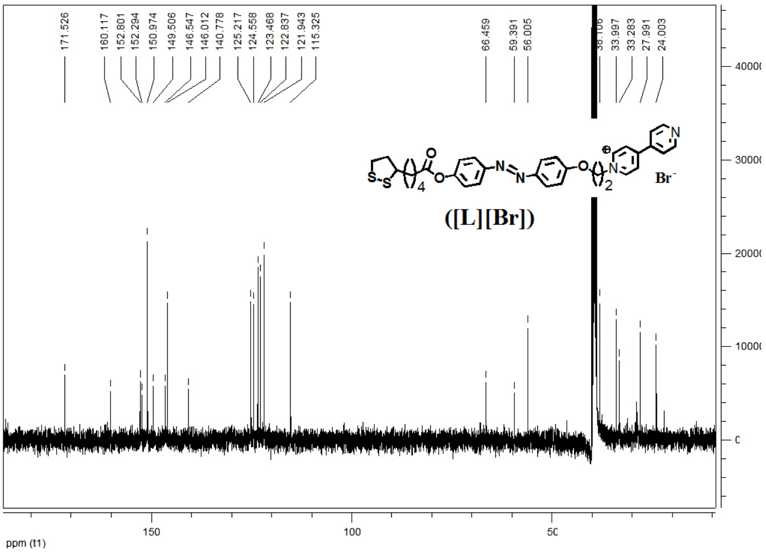
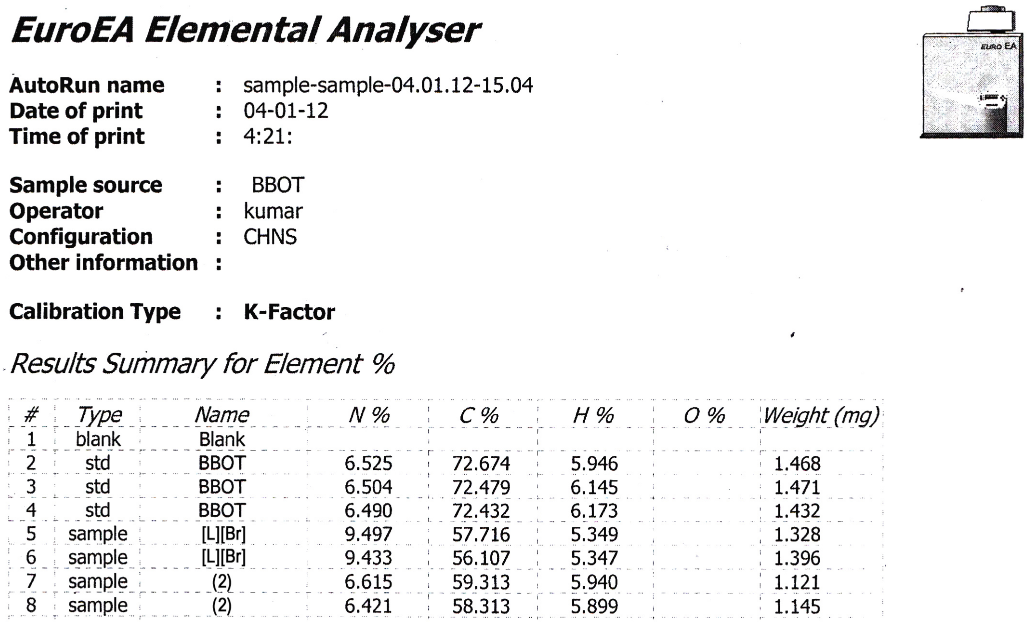


Fig. S18 ^{13}C NMR spectrum of the compound [L][Br].

Elemental Analysis Reports for Compounds 2 and [L][Br]



EuroEA Elemental Analyser

AutoRun name : sample-sample-04.01.12-15.04
Date of print : 04-01-12
Time of print : 4:21:

Sample source : BBOT
Operator : kumar
Configuration : CHNS
Other information :

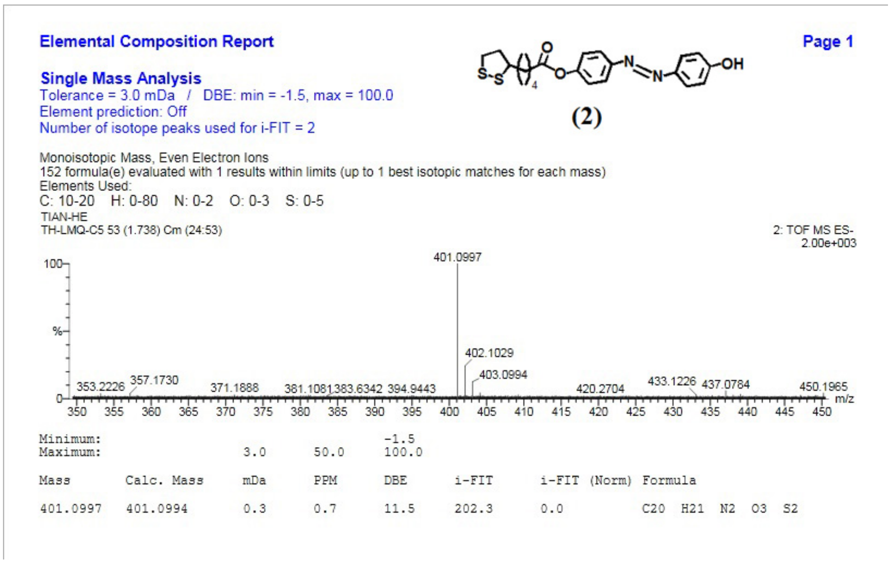
Calibration Type : **K-Factor**

Results Summary for Element %

#	Type	Name	N %	C %	H %	O %	Weight (mg)
1	blank	Blank					
2	std	BBOT	6.525	72.674	5.946		1.468
3	std	BBOT	6.504	72.479	6.145		1.471
4	std	BBOT	6.490	72.432	6.173		1.432
5	sample	[L][Br]	9.497	57.716	5.349		1.328
6	sample	[L][Br]	9.433	56.107	5.347		1.396
7	sample	(2)	6.615	59.313	5.940		1.121
8	sample	(2)	6.421	58.313	5.899		1.145

Fig. S19 Elemental analysis reports of the compounds **2** and [L][Br].

Elemental Composition Reports for Compounds 2, 3 and [L][Br]



Elemental Composition Report **Page 1**

(2)

Single Mass Analysis
Tolerance = 3.0 mDa / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 2

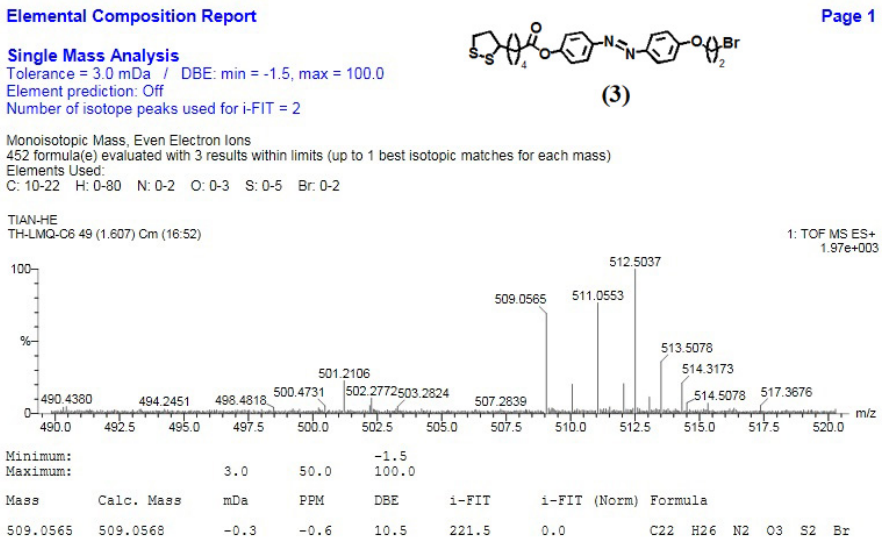
Monoisotopic Mass, Even Electron Ions
152 formula(e) evaluated with 1 results within limits (up to 1 best isotopic matches for each mass)
Elements Used:
C: 10-20 H: 0-80 N: 0-2 O: 0-3 S: 0-5
TIAN-HE
TH-LMQ-C5 53 (1.738) Cm (24:53)

```
Minimum:                                  -1.5
Maximum:                  3.0      50.0   100.0

Mass       Calc. Mass     mDa      PPM    DBE     i-FIT     i-FIT (Norm) Formula

401.0997   401.0994       0.3      0.7    11.5    202.3     0.0          C20  H21  N2  O3  S2
```

Fig. S20 Single mass analysis of the compound **2**.



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(3)

Single Mass Analysis
Tolerance = 3.0 mDa / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions
452 formula(e) evaluated with 3 results within limits (up to 1 best isotopic matches for each mass)
Elements Used:
C: 10-22 H: 0-80 N: 0-2 O: 0-3 S: 0-5 Br: 0-2

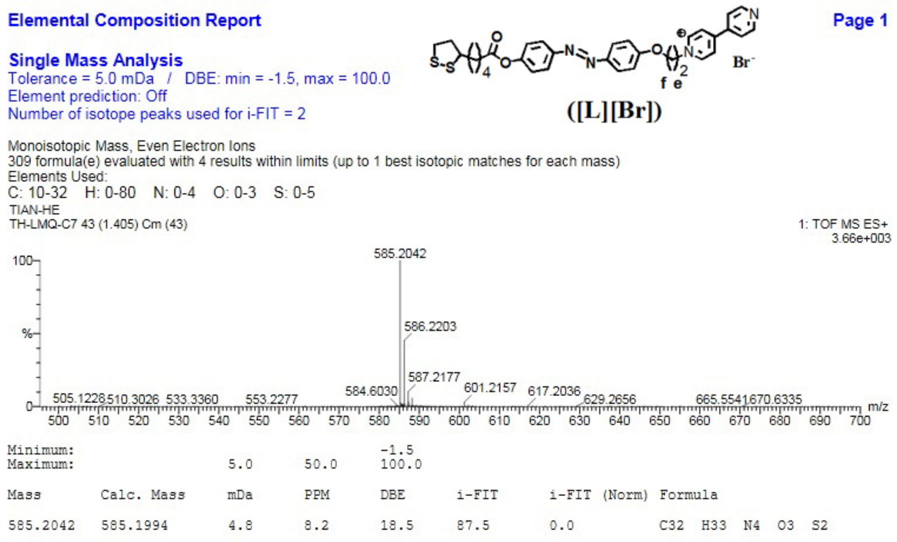
TIAN-HE
TH-LMQ-C6 49 (1.607) Cm (16:52)

```
Minimum:                                  -1.5
Maximum:                  3.0      50.0   100.0

Mass       Calc. Mass     mDa      PPM    DBE     i-FIT     i-FIT (Norm) Formula

509.0565   509.0568       -0.3     -0.6   10.5    221.5     0.0          C22  H26  N2  O3  S2  Br
```

Fig. S21 Single mass analysis of the compound **3**.



Elemental Composition Report

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Single Mass Analysis
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions
309 formula(e) evaluated with 4 results within limits (up to 1 best isotopic matches for each mass)
Elements Used:
C: 10-32 H: 0-80 N: 0-4 O: 0-3 S: 0-5
TIAN-HE
TH-LMQ-C7 43 (1.405) Cm (43)

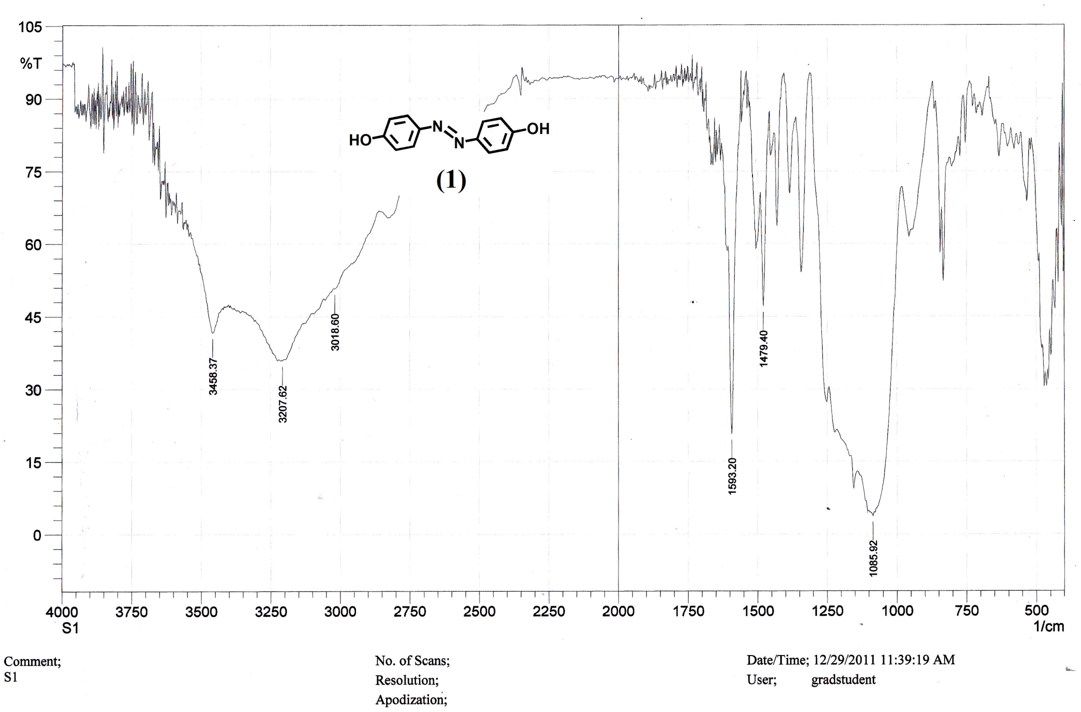
```
Minimum:                      -1.5
Maximum:          5.0   50.0  100.0

Mass      Calc. Mass  mDa   PPM   DBE   i-FIT  i-FIT (Norm)  Formula

585.2042  585.1994    4.8   8.2   18.5  87.5   0.0           C32  H33  N4  O3  S2
```

Fig. S22 Single mass analysis of the compound [L][Br].

FT-IR Spectra for Compounds 1, 2, 3 and [L][Br]



Comment;
S1

No. of Scans;
Resolution;
Apodization;

Date/Time; 12/29/2011 11:39:19 AM
User; gradstudent

Fig. S23 FT-IR spectrum of the compound **1**.

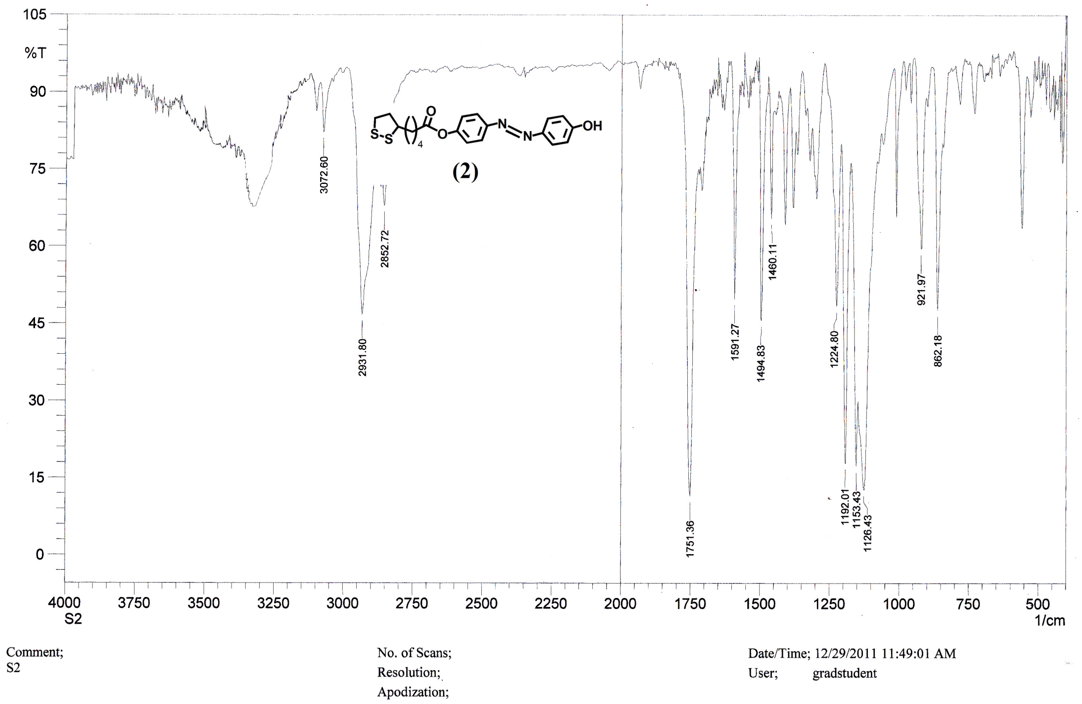


Fig. S24 FT-IR spectrum of the compound **2**.

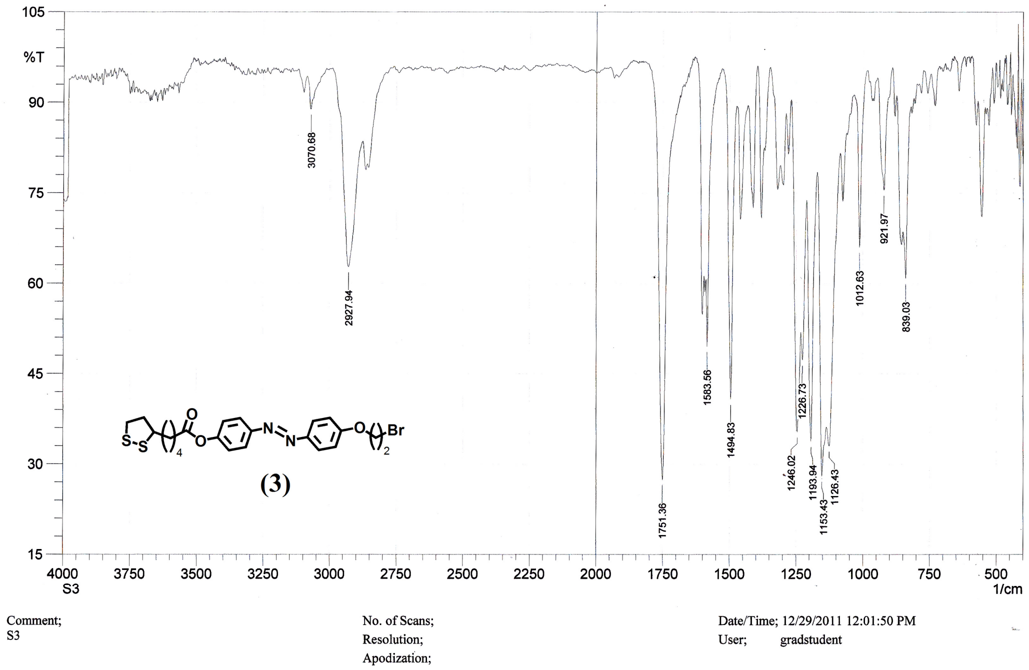


Fig. S25 FT-IR spectrum of the compound **3**.

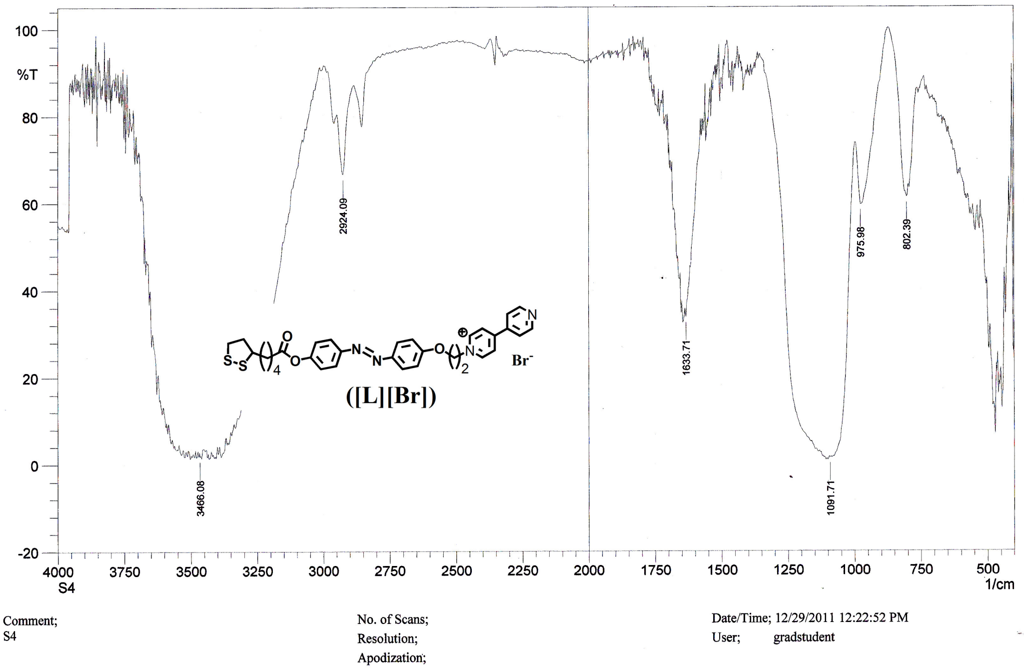


Fig. S26 FT-IR spectrum of the compound [L][Br].

References:

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