Electronic Supplementary Information for Nanoscale

Coordination-directed self-assembly of molecular motor: towards a two-wheel drive nanocar

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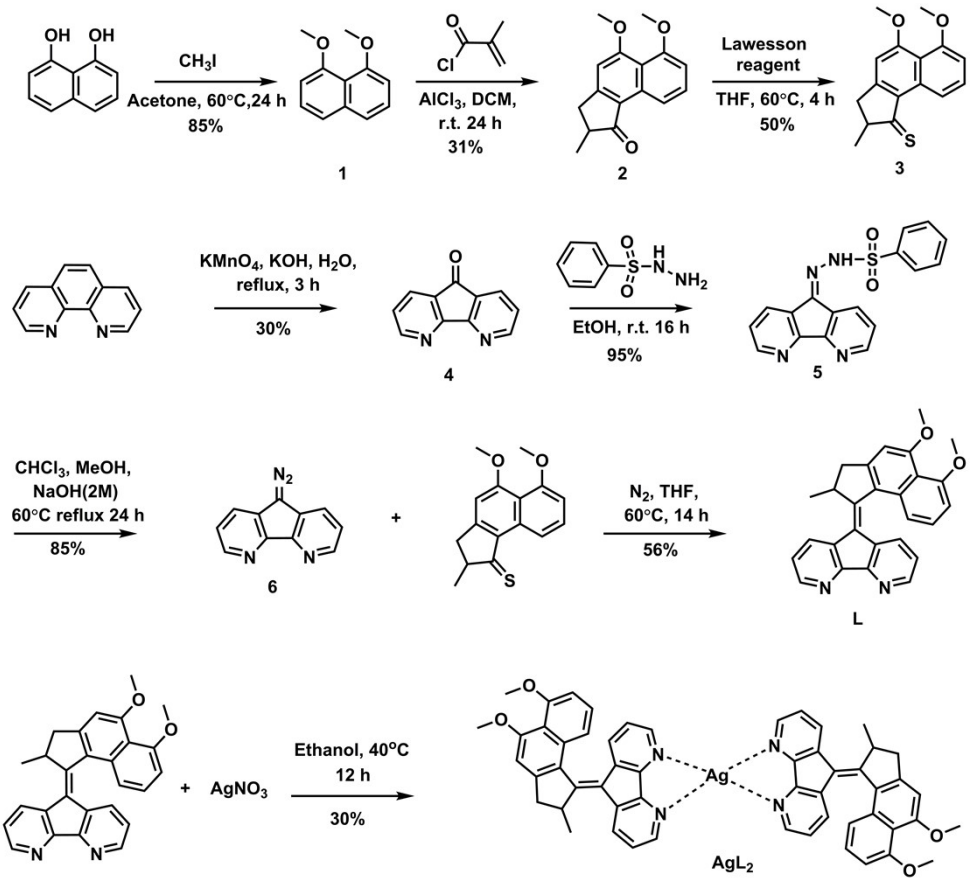
1. Synthesis



Scheme S1. Synthesis of overcrowded alkene-based ligand motor **L** and its silver complex $\mathbf{AgL_2}$.

Synthetic procedure

1,8-dimethoxynaphthalene (1)

1,8-dihydroxynaphthalene (0.8 g, 5 mmol) was dissolved in acetone (20 mL), then K_2CO_3 (3.46 g, 25 mmol) and methyl iodide (1.56 mL, 25 mmol) was added to the solution sequentially. The reaction mixture was refluxed for 24 h. The progress of the reaction was monitored by thin-layer chromatography. At the end of the reaction, the solution was acidified with dilute HCl (2 M, 20 mL) and extracted with CH_2Cl_2 (3 × 20 mL). The combined organic phases were washed with water and saturated NaCl, then dried over $MgSO_4$, and concentrated under vacuum. Finally, the pure product was obtained through further silica gel column chromatography (petroleum ether: ethyl acetate = 9:1). (light grey solid, 0.8 g, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.34 (m, 4H), 6.86 (dd, J = 7.7, 3.9 Hz, 2H), 3.98 (s, 6H) ppm. ESI-MS (CH_3OH, m/z): 189.0899 ([M + H]$^+$, calcd for $[C_{12}H_{13}O_2]^+$: 189.0916).

5,6-dimethoxy-2-methyl-2,3-dihydro-1H-cyclopenta[a]naphthalen-1-one (2)

A mixture of $AlCl_3$ (1.33 g, 10 mmol) and methacryloyl chloride (0.48 mL, 5 mmol) in

degassed CH_2Cl_2 (25 mL) was cooled down to -78 °C, solid complex **1** (0.94 g, 5mmol) was poured into the mixture portion wise over 10 minutes, then the mixture was allowed to attain room temperature overnight. After the reaction completed, the solution was poured into a mixture of 25 mL ice water and 12.5 mL HCl (1 M), continue stirring for 4 h, the resulting mixture was extracted with diethyl (3 × 25 mL), the combined organic layer was washed with brine (20 mL), dried over $MgSO_4$, and the crude product was purified by silica gel column chromatography (petroleum ether: ethyl acetate = 9:1) to give the corresponding product (yellow solid, 0.4 g, 31%). ESI-MS (CH_3OH, m/z): 257.1150 ($[M + H]^+$, calcd for $[C_{16}H_{17}O_3]^+$: 257.1172), 535.2048 ($[2M + Na]^+$, calcd for $[C_{32}H_{32}NaO_6]^+$: 535.2097).

5,6-dimethoxy-2-methyl-2,3-dihydro-1H-cyclopenta[a]naphthalene-1-thione (3)

Compound **2** (160 mg, 0.62 mmol) was dissolved in dry THF (10 mL), then Lawesson Reagent (506 mg, 1.25 mmol) was added to the solution, the mixture stirred for 4 h at 60 °C, after that the solvent was removed in vacuum, and the crude product was purified by silica gel column chromatography (petroleum ether: ethyl acetate = 10:1) to give the corresponding product (orange powder, 85 mg, 50%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.01 (m, 1H), 7.64 (t, *J* =10.4 Hz, 1H), 7.00 (d, *J* = 7.1 Hz, 1H), 6.82 (s, 1H), 4.08 (s, 3H), 3.97 (s, 3H), 3.49-3.37 (m, 1H), 3.14 (m, 1H), 2.91-2.78 (m, 1H), 1.48 (d, *J* = 8.0 Hz, 3H). ESI-MS (CH_3OH, m/z): 273.0940($[M + H]^+$, calcd for $[C_{16}H_{17}O_2S]^+$: 273.0949).

Compounds **4-6** were prepared according to literature procedures. [S1]

5-(5,6-dimethoxy-2-methyl-2,3-dihydro-1*H*-cyclopenta[a]naphthalen-1-ylidene)-5*H*-cyclopenta[2,1-*b*:3,4-*b'*]dipyridine. ((±)-L)

Freshly prepared **3** (250 mg, 1.28 mmol) and compound **6** (200 mg, 0.7 mmol) in THF (20 mL) were heated at reflux for 14 h under a N_2 atmosphere. The solution was naturally cooled to room temperature, followed by concentration, and the crude product was purified by silica gel column chromatography (petroleum ether : ethyl acetate = 10:1, followed by EA:DCM=4:1) to give the corresponding product (yellow solid, 160 mg, 56%).^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.67 (d, *J* =4.5 Hz, 1H), 8.52 (d, *J* =4.4 Hz, 1H), 8.30 (d, *J* =7.7 Hz, 1H), 7.41 (dd, *J* =7.5, 4.8 Hz, 1H), 7.21 (m, 2H), 7.00 (s, 1H), 6.96-6.84 (m, 3H), 4.24 (m, 1H), 4.06 (s, 3H), 3.99 (s, 3H), 3.56 (dd, *J* =15.4, 5.7 Hz, 1H), 2.79 (d, *J* =16.2 Hz, 1H), 1.42 (d, *J* =7.7 Hz, 3H). ^{13}C NMR (100 MHz, CD_2Cl_2) δ 161.22, 158.34, 156.85, 155.91, 155.45, 150.90, 147.66, 147.45, 134.44, 133.17, 132.66, 131.90, 130.66, 128.10, 127.34, 122.56, 121.37, 121.23, 119.43, 116.31, 106.33, 103.77, 56.28, 56.24, 44.57, 41.79, 19.65. ESI-MS (CH_3OH, m/z) 407.1737 ($[L+H]^+$, calcd for $[C_{27}H_{23}N_2O_2]^+$: 407.1760), 835.3233 ($[2L+Na]^+$, calcd for $[C_{54}H_{44}N_4O_4Na]^+$: 835.32 60).

2. Literature research

Table S1. Strategies of regulating the excitation wavelength of 2nd generation molecular motors

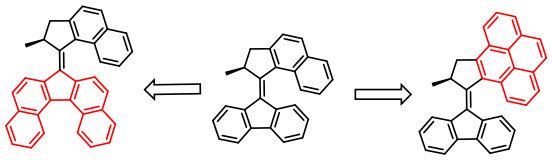
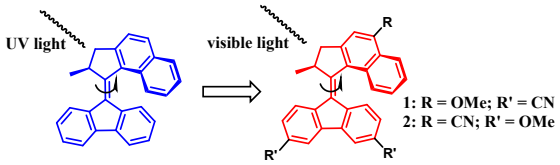
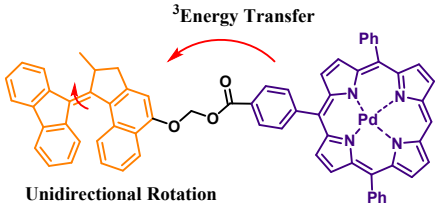
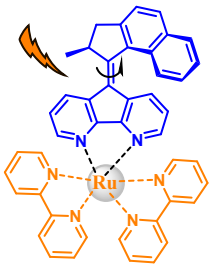
Approaches	Structure	λ_{ex} (solvent)	Literature
Extension of π-system		490 nm (DCM)	*Org. Lett.* **2017**, *19*, 1402-1405; *Helv. Chim. Acta.* **2019**, *102*, e1800221
Construction of "push-pull" system		530 nm (DCM)	*Chem. Sci.* **2019**, *10*, 8768-8773
Triplet-triplet sensitization		532 nm (1,2-dichloroethane)	*J. Am. Chem. Soc.* **2012**, *134*, 17613-17619
Coordinate with Ru(II)		450 nm (DCM)	*Angew. Chem. Int. Ed.* **2015**, *127*, 11619-11623.

Table S2. Approaches of modulating rotate speed of 2nd generation molecular motors

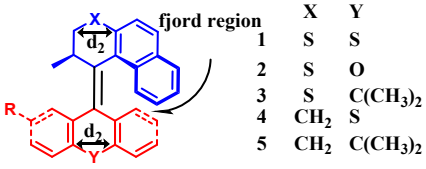
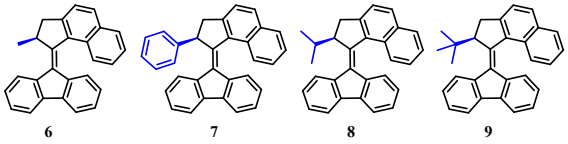
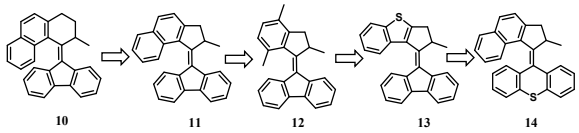
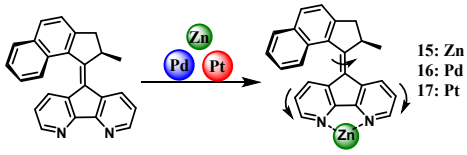
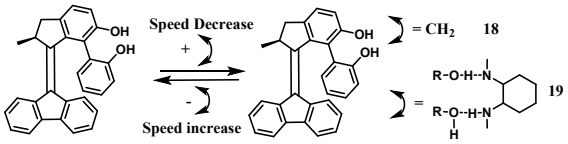
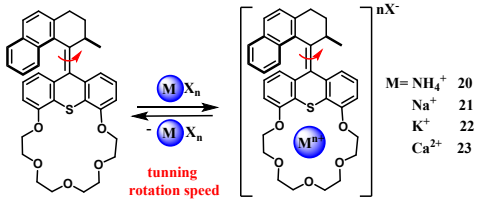
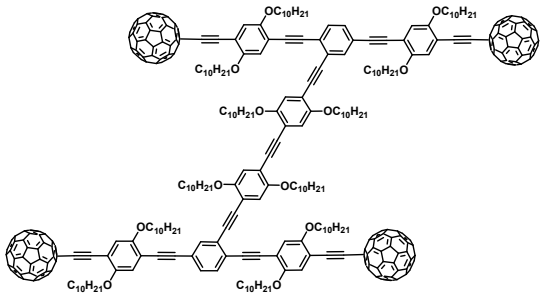
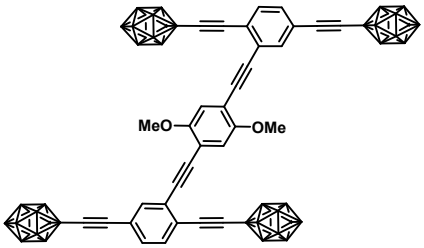
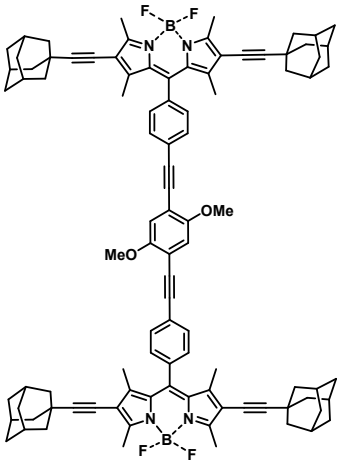
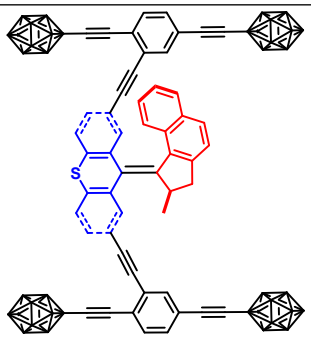
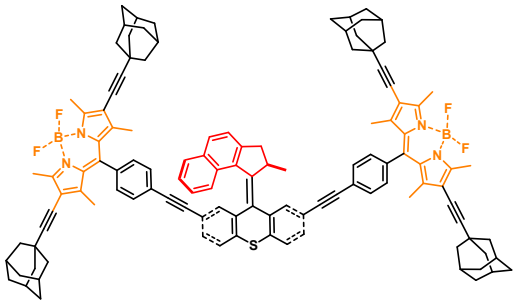
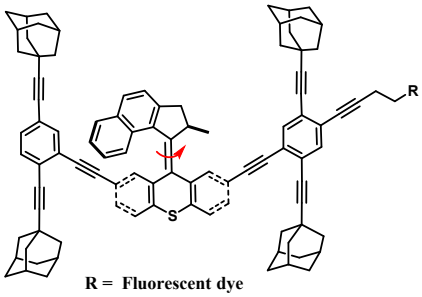
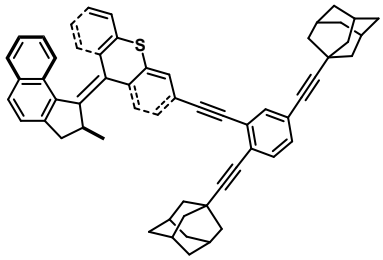
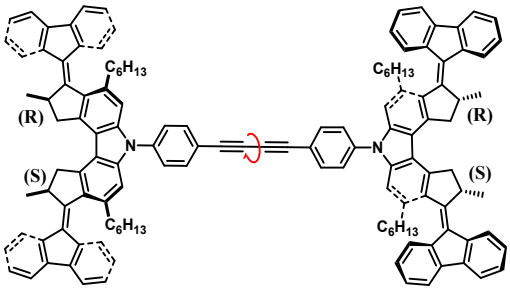
Approaches	Structure	$t_{1/2}$ for THI	Literature
Exchanging the size of bridging atoms		**1**: 215 h **2**: 26.3 h **3**: 233 h **4**: 0.67 h **5**: 2.01 h (hexane)	*J. Am. Chem. Soc.* **2002**, *124*, 5037-5051
Introducing bulky substituent at the stereogenic center		**6**: 190 s **7**: 587 s **8**: 95 s **9**: 5.74×10^{-3} s (hexane)	*J. Am. Chem. Soc.* **2006**, *128*, 5127-5135
Contraction of the ring		**10**: 1400 year **11**: 3.2 min **12**: 15 s **13**: 70 ms **14**: 1.1×10^{2} ns (iso-pentane)	*Chem. Soc. Rev.* **2017**, *46*, 2592-2621
Using the principles of allosteric effect		**15**: 38 s **16**: 9.8 s **17**: 2.7 s (DCM)	*J. Am. Chem. Soc.* **2016**, *138*, 13597-13603
Through covalent and noncovalent binding.		**18**: 5×10^{3} s **19**: 30 s (DCM)	*Chem. Eur. J.* **2017**, *23*, 1-5
Through host-guest non-covalent interaction		**20**: 12.4 min **21**: 7.6 min **22**: 9.1 min **23**: 7.1 min (CH_3CN)	*Org. Lett.* **2018**, *20*, 3715- 3718

Table S3. Representative artificial "four-wheels nanocar"

Category	Structure	Literature
Nanocar without motor		*Nano Lett.*, **2005**, *5*, 2330-2334.
		*Acc. Chem. Res.*, **2009**, *42*, 473-487.
		*ACS Nano.*, **2013**, *7*, 35-41
Motorized nanocar with *p*-carborane as the wheels		*ACS Nano.*, **2012**, *6*, 592-597.

Fluorescent motorized nanocar		*Asian. J. Org. Chem.* **2015**, *4*, 1308-1314
Motorized nanocar which can translate on a Cu(111) surface upon light activation	 	*Tetrahedron,* **2017**, *73*, 4864-4873. *ACS Nano*, **2016**, *10*, 10945-10952.
Motorized nanocar which can move directionally across Cu(111) surface after electronic excitation		*Nature,* **2011**, *479,* 208-201.

3. UV-Vis characterization of photochemical and THI Process

3.1 The selection of excitation wavelength on L and AgL_2

A xenon lamp light source (Perfect light, PLS-SXE300) which was equipped with different optical filters (365 nm to 700 nm) and power meter (PLS-MW2000) was used for photoisomerization studies and measuring the radiant power of the incident excitation beams at the excitation wavelength. The radiant power was obtained in mW, then the value was transformed into photo intensity (***I***), which was obtained in mW/cm^2 and was further used for quantum yield calculation.

To select a suitable wavelength that can excite the sample **L** and $\mathbf{AgL_2}$, we conducted selection experiments of **L** and $\mathbf{AgL_2}$ in dry DCM solution (4×10^{-5} M) under different excitation wavelength**.** The solution of **L** and $\mathbf{AgL_2}$ was exposed to different light source (365 nm to 450 nm for **L**; 450-500 nm for $\mathbf{AgL_2}$), then utilized the UV-VIS-NIR spectrophotometer to monitor the changes of UV-Vis spectrum upon irradiation (Figure S1).

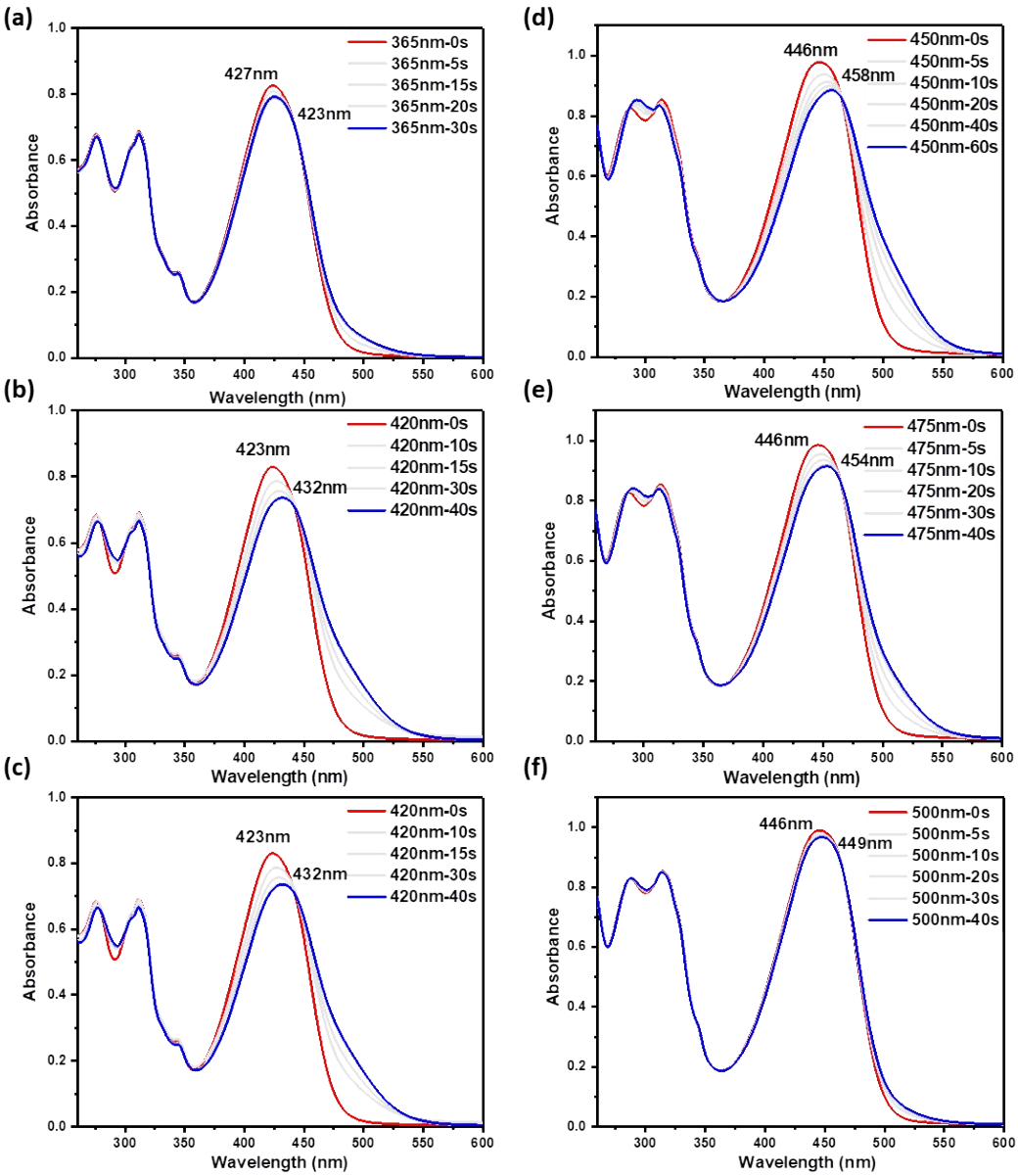


Figure S1. UV-Vis spectrum of photoisomerization process of **L** (a-c) and $\mathbf{AgL_2}$ (d-f) in dry DCM (4×10^{-5} M) under different excitation wavelength (a-f: 365 nm, 420 nm, 450 nm, 475 nm, 500 nm).

3.2 Calculation of quantum yields

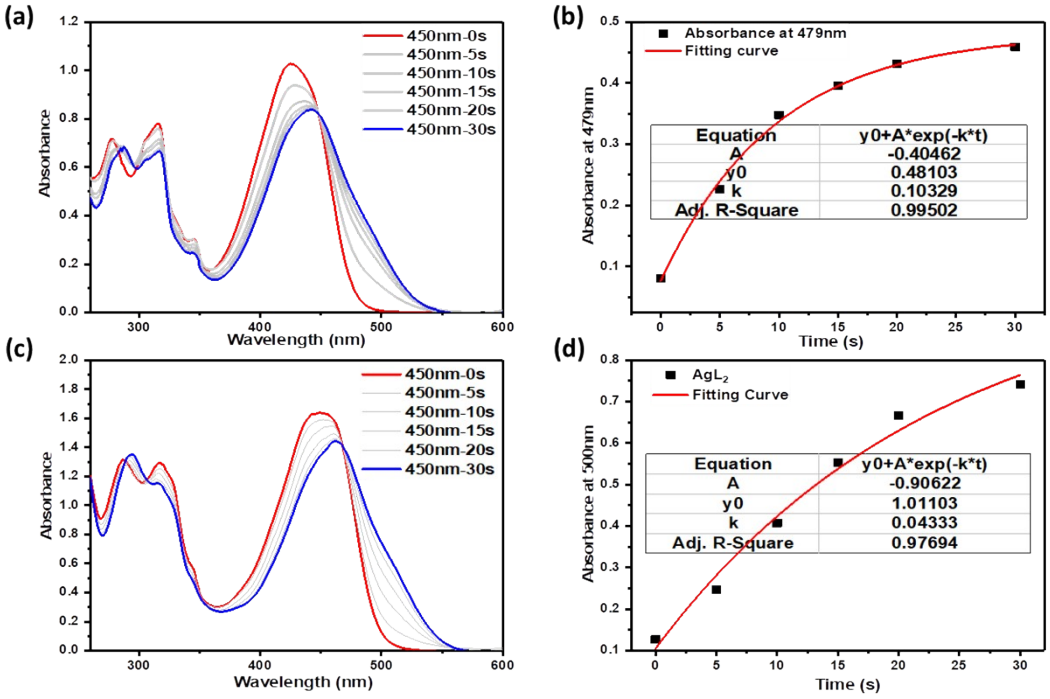


Figure S2. Kinetics for the photoisomerization (irradiation at 450 nm) of **L** and **AgL$_2$** in dry DCM (4×10^{-5} M) at 250 K. The plot figure b and d is of the absorbance changes of **L** (at 479 nm) and **AgL$_2$** (at 500 nm) as a function of time. The photoisomerizatio rate constant $k_{\text{stable-unstable}}$ was used for quantum yield calculations.

The quantum yields of photo-isomerization reactions was measured following the reported literature.[S2] Firstly, the solution of **L** and **AgL$_2$** in DCM(4×10^{-5} M) were prepared to monitor UV-Vis absorption spectrum under irradiation of 450 nm at 250 K through Agilent Cary 6000i UV-VIS-NIR spectrophotometer (Figure S2 (a) and (c)). For ligand **L**, it was exposed to xenon lamp light source equipped with 450 nm filter, monitored the absorbance changes against irradiation time; then the maximum of absorbance difference (**L** at 479 nm, **AgL$_2$** at 500 nm) was monitored and plotted against time affording the photo-dynamic profile of light-induced stable motor to unstable one (Figure S2 (b) and (d)). After that, the experimental curve is fitted to the monoexponential function ($Y=Y_0+A\times\exp(-k\times t)$.) so as to obtain the rate constant ($k_{\text{stable -unst}}$) of photo-isomerization process. Then the rate constant was employed to calculate the quantum yield according to the following equations **1-4**. Among which, σ_{ex} (cm^2/molecule) is the absorption cross-section at excitation wavelength λ_{ex} (nm). Ψ_{ex} is the photon flux. I (W/cm^2) is the optical intensity of irradiation light performed on the sample, N_a is the Avogadro's constant, and κ_{ex} is the rate constant for absorption at excitation wavelength. The relative optical parameters are listed in Table S4; From these values and equations **1-4**, the quantum yield ($\Phi_{\text{stable-unstable}}$) of photochemical process was obtained.

$$\sigma_{ex}=(10^3\times\ln(10/N_a)\times\varepsilon_{ex} \quad (1)$$

$$\Psi_{ex}=5\times10^{15}\times\lambda_{ex}\times I \quad (2)$$

$$\kappa_{ex}=\sigma_{ex}\times\Psi_{ex} \quad (3)$$

$$\Phi_{stable\text{-}unstable}=k_{stable\text{-}unstable}/\kappa_{ex} \quad (4)$$

Table S4. Relative optical parameters for calculating the quantum yields

Complexes	λ_{ex} (nm)	ε_{ex} (L/(mol*cm))	I (mW/cm^2)	Ψ_{ex} (/10^{16})	σ_{ex} (×10^{17})	$k_{stable\text{-}unstable}$	k_{ex}	Φ (stable-unstable) (%)
L	450	20213	39	8.79	7.73	0.103	6.8	1.5
AgL_2		33663			1.29	0.0433	11.32	0.38

3.3 Kinetic Studies of THI process

Since the thermal half-lives of **L** and **AgL_2** for THI process is very short at room temperature, the kinetics of this process were studied at 265 K and monitored through Agilent Cary 6000i UV-VIS-NIR spectrophotometer. They were dissolved in dry DCM (4×10^{-5} M) and irradiated to PSS with 450nm light source, the light source was removed and the sample was remained at 265 K under darkness, meanwhile the absorbance changes against time was recorded (Figure S3a and S3c).

Changes in the absorbance at 476nm for **L** and 500nm for **AgL_2** were monitored to afford decay profile of THI process (Figure S3b and S3d). The rate constant (k_1) of the first order decay at 265 K was determined by fitting the decay curve to the equation $Y=Y_0+A\times\exp(-k/t)$ using Origin software.

The value of k_1 (265 K) was measured and then used to calculate the energy barriers for the thermal helix inversion process using the Eyring equation (Eq. 5.). With the energy barriers ($\Delta G^{\ddagger}$) in hand, the Arrhenius equation (Eq. 6) was used to extrapolate the rate constants (k_2) at 293 K, from which the room-temperature thermal half-lives were determined [S3]. The relative parameter refers to calculate the $\Delta G^{\ddagger}$ (293 K) are listed in Table S5.

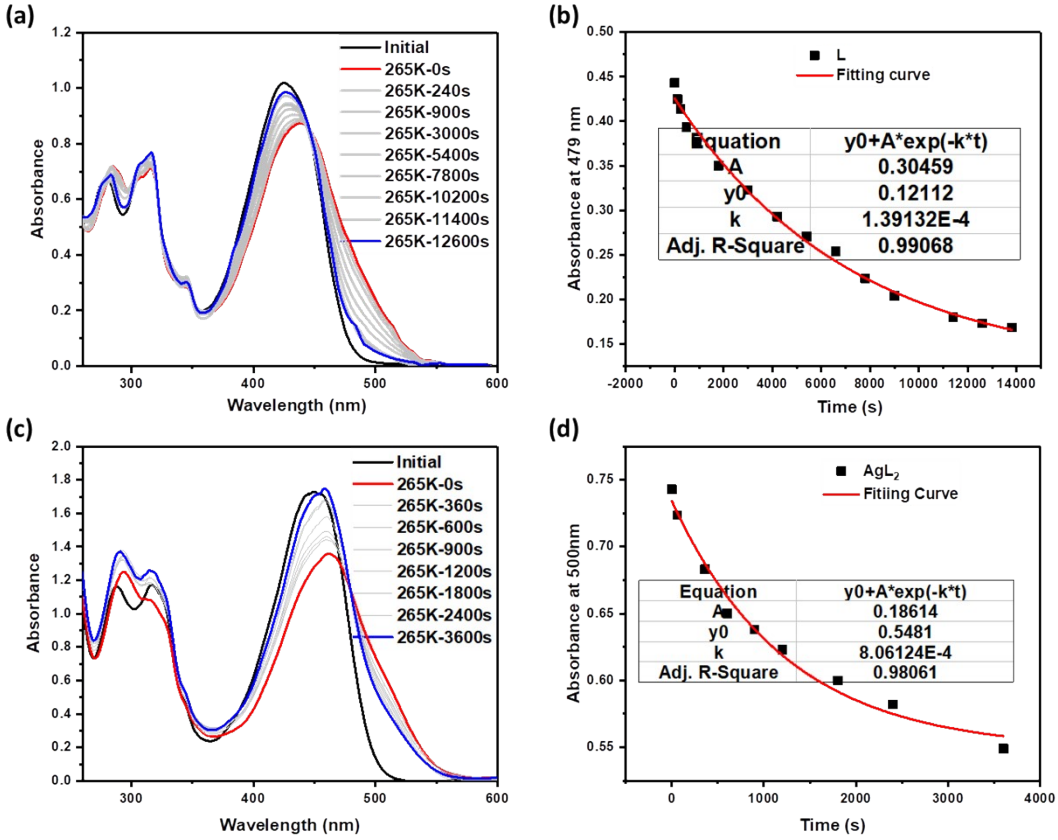


Figure S3. Thermal helix inversion of **L** and **AgL_2** in dry DCM at 265 K. The plot is of the absorbance changes of **L** (at 476 nm) and **AgL_2** (at 500 nm) as a function of time. The resulting k_1 value was calculated through fitted with monoexponential functions $Y=Y_0+A\times\exp(-k/t)$.

$$\Delta G^{\ddagger}=8.314\times T\times[23.760+\ln(T/K) \qquad (5)$$

$$\ln(k_2/k_1)=\Delta G^{\ddagger}/R\times[(1/T_1)-(1/T_2)] \qquad (6)$$

Table S5. The kinetic parameters of L and AgL_2 for THI process

Complex	T_1(K)	T_2(K)	k_1(265K) s^{-1}	$\Delta G^{\ddagger}$ (kJ/mol)	k_2(293K) s^{-1}	$t_{1/2}$(293K) (s)
L	265	293	0.00014	84	0.0053	130.3
AgL_2	265	293	0.000806	80.1	0.0260	26.6

3.4 Studies on fatigue resistance

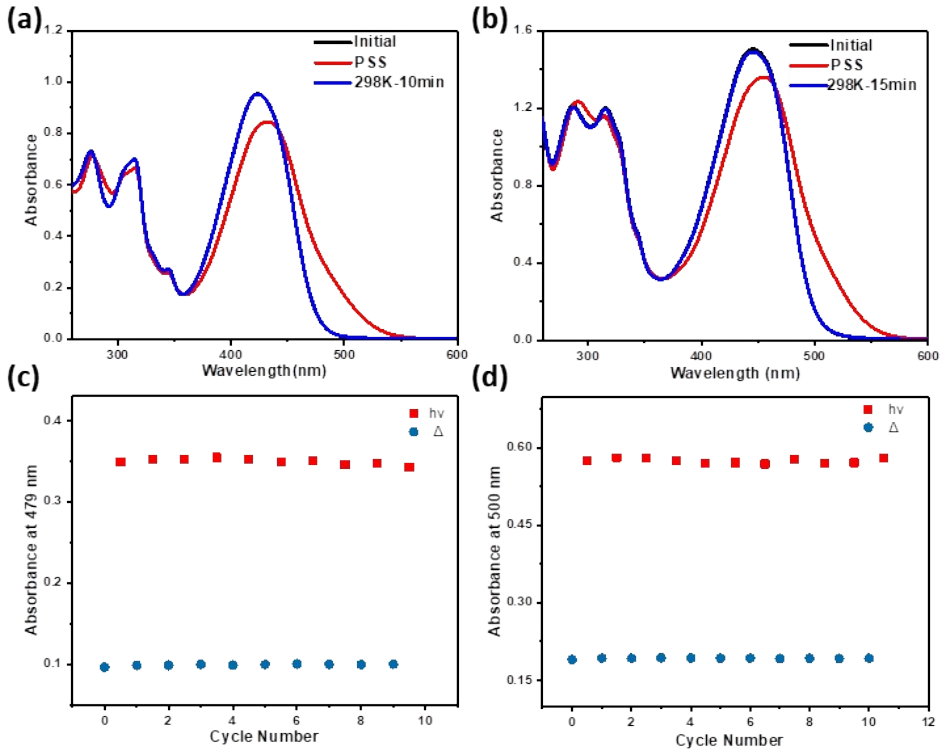


Figure S4. Isomerization behavior of (a) **L**; (b) $\mathbf{AgL_2}$ at 298 K and fatigue-resistance studies of (c) **L** and (d) $\mathbf{AgL_2}$. The absorbance change at 479 nm and 500 nm was monitored for **L** and $\mathbf{AgL_2}$, respectively.

3.5 Disassembly process of "two-wheel nanocar" monitored by UV-Vis spectroscopy

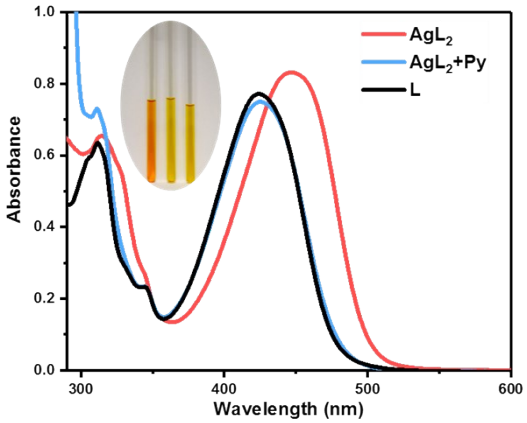


Figure S5. Disassembly process of $\mathbf{AgL_2}$ monitored through UV−Vis spectroscopy. Spectra of $\mathbf{AgL_2}$ (2×10^{-5} M) in DCM solution (pink line); after addition of pyridine (blue line) and **L** (2×10^{-5} M) in DCM solution (black line). Insert: The color of $\mathbf{AgL_2}$, after addition of pyridine ($\mathbf{AgL_2}$**-Py**), **L**. (from left to right)

4 Fluorescence characterization

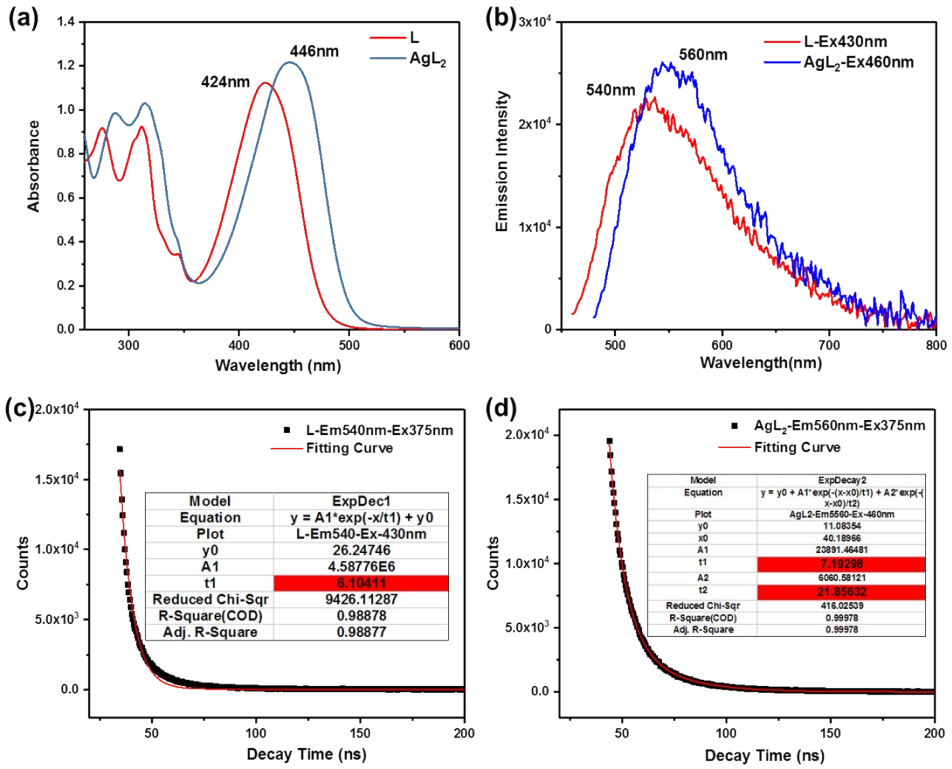


Figure S6. Spectrum of **L** and **AgL_2** measured in DCM (4×10^{-5} M) solution at 200 K. (a) UV-Vis absorption spectrum; (b) Emission spectrum (λ_{ex}=430 nm and 460 nm); Emission decay behaviors of (c) **L** and (d) **AgL_2** (under excitation of 375 nm laser).

5 NMR, ESI-MS and IR characterization

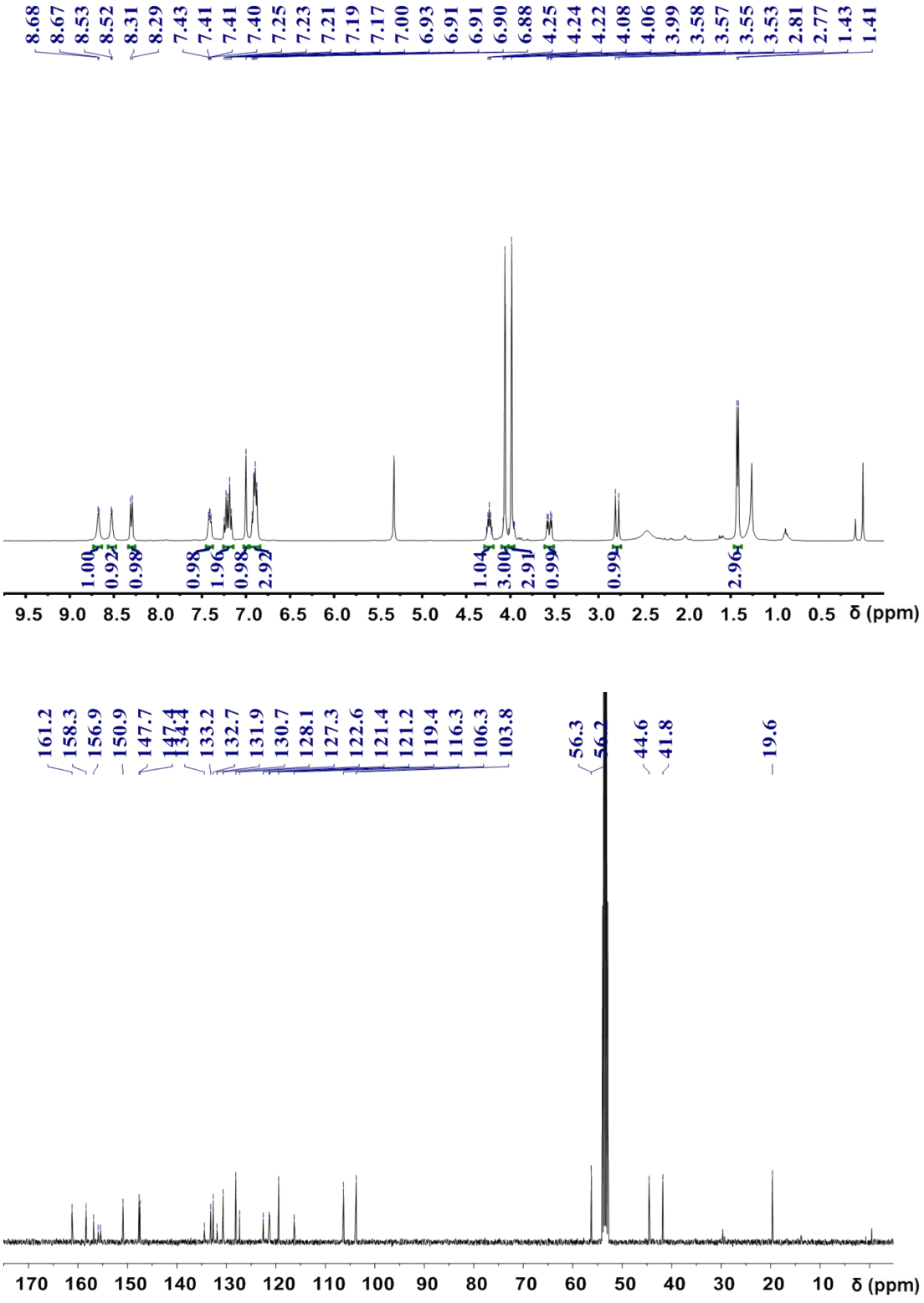


Figure S7. ^{1}H NMR (400 MHz) (top) and ^{13}C NMR (100 MHz) (bottom) spectra of **L** measured in CD_2Cl_2 at 298 K.

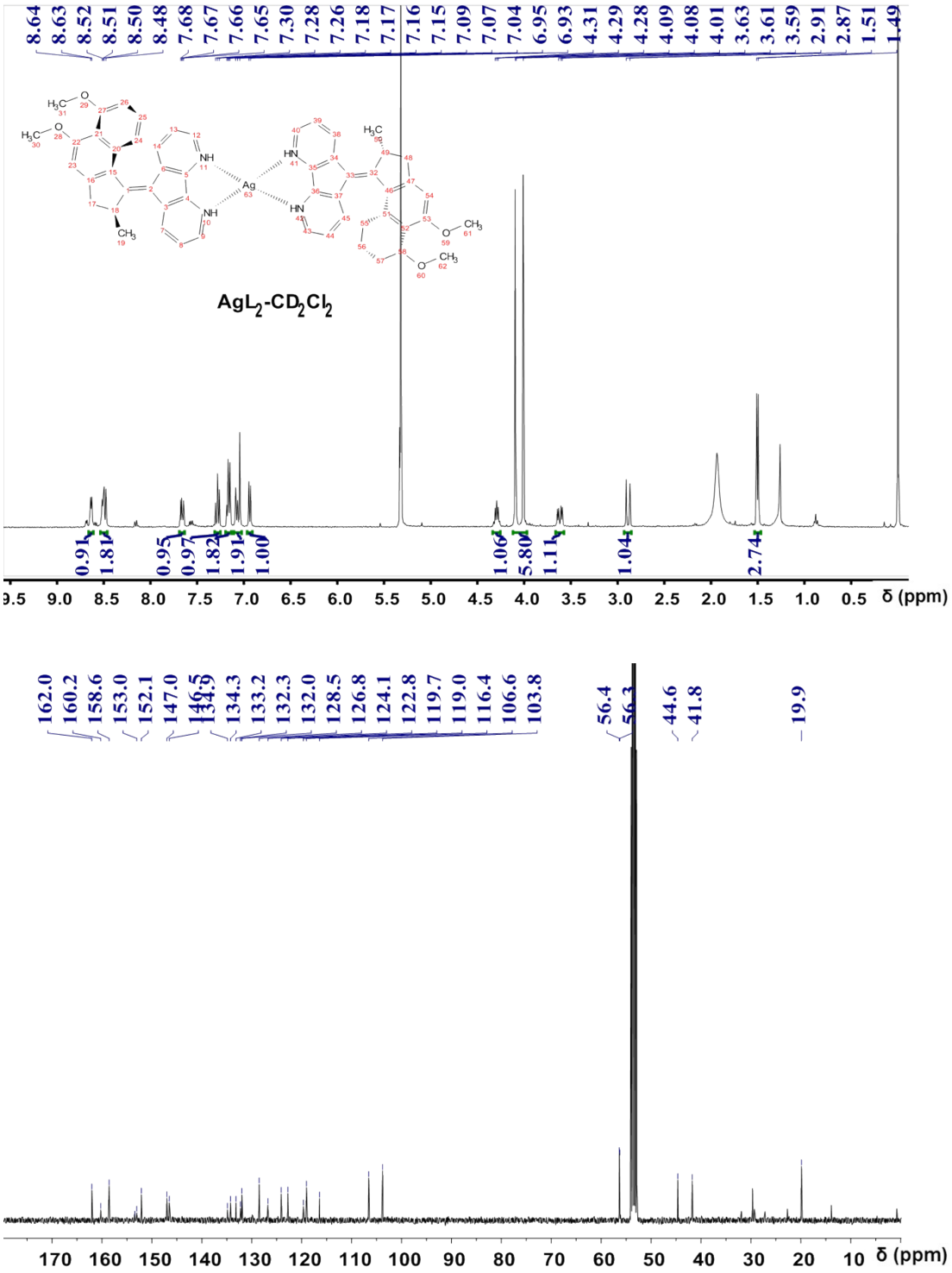


Figure S8. ^{1}H NMR (400 MHz) (top) and ^{13}C NMR (100 MHz) (bottom) spectra of **AgL_2** measured in CD_2Cl_2 at 298 K.

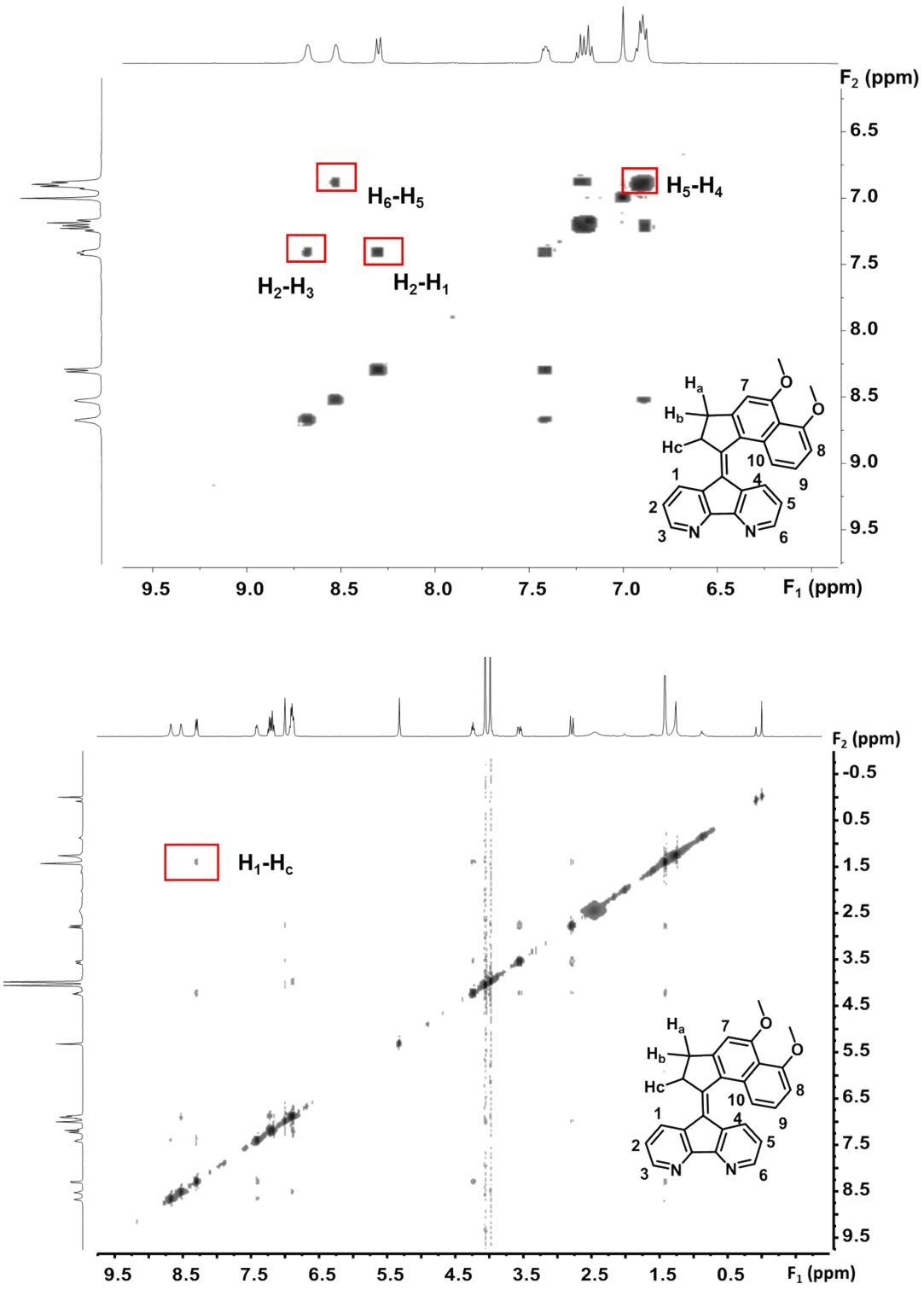


Figure S9. COSY (top) and **NOESY** (bottom) spectrum of **L** measured in CD_2Cl_2 at 298 K.

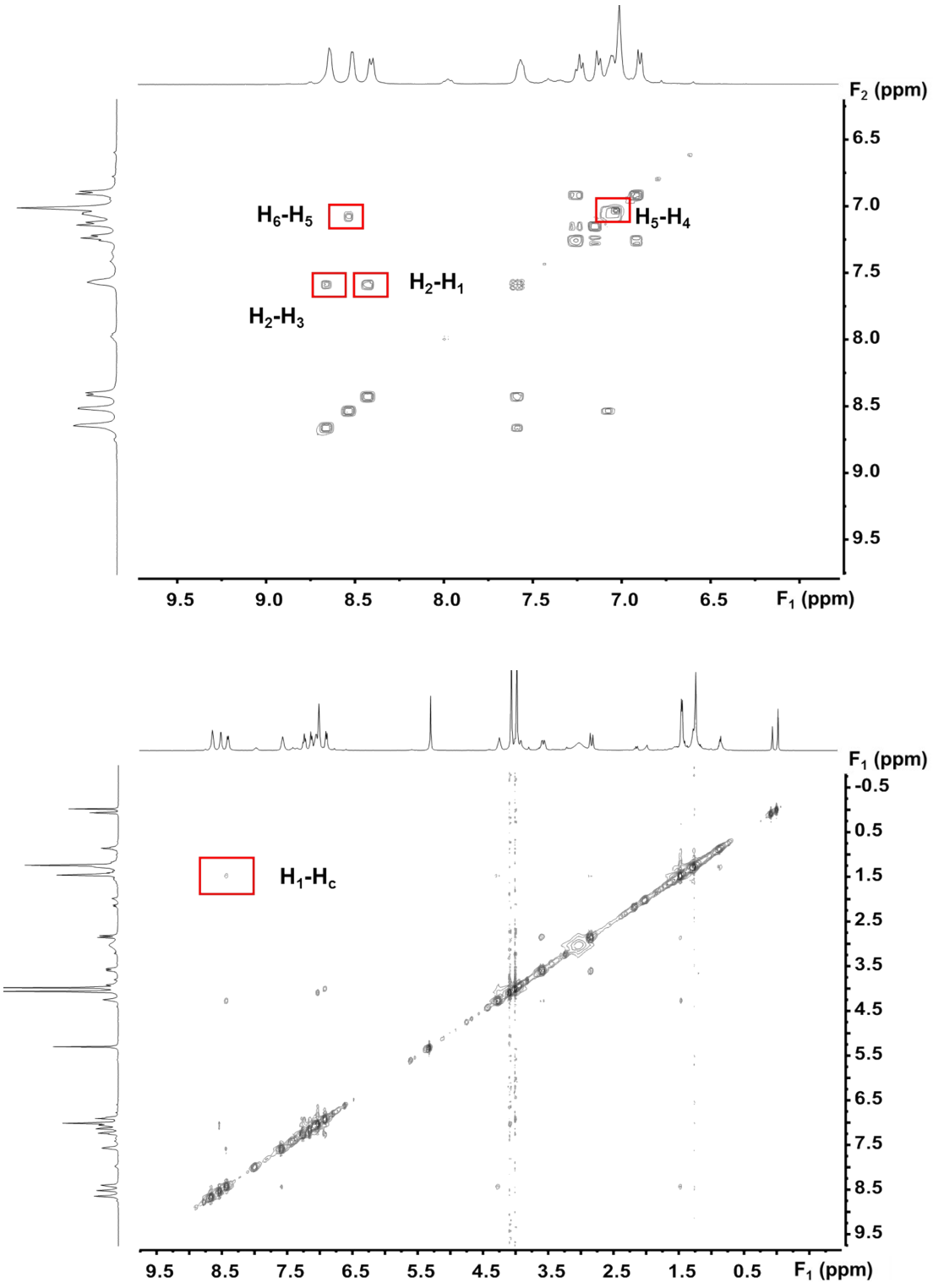


Figure S10. COSY (top) and **NOESY** (bottom) spectrum of **AgL_2** measured in CD_2Cl_2 at 298 K.

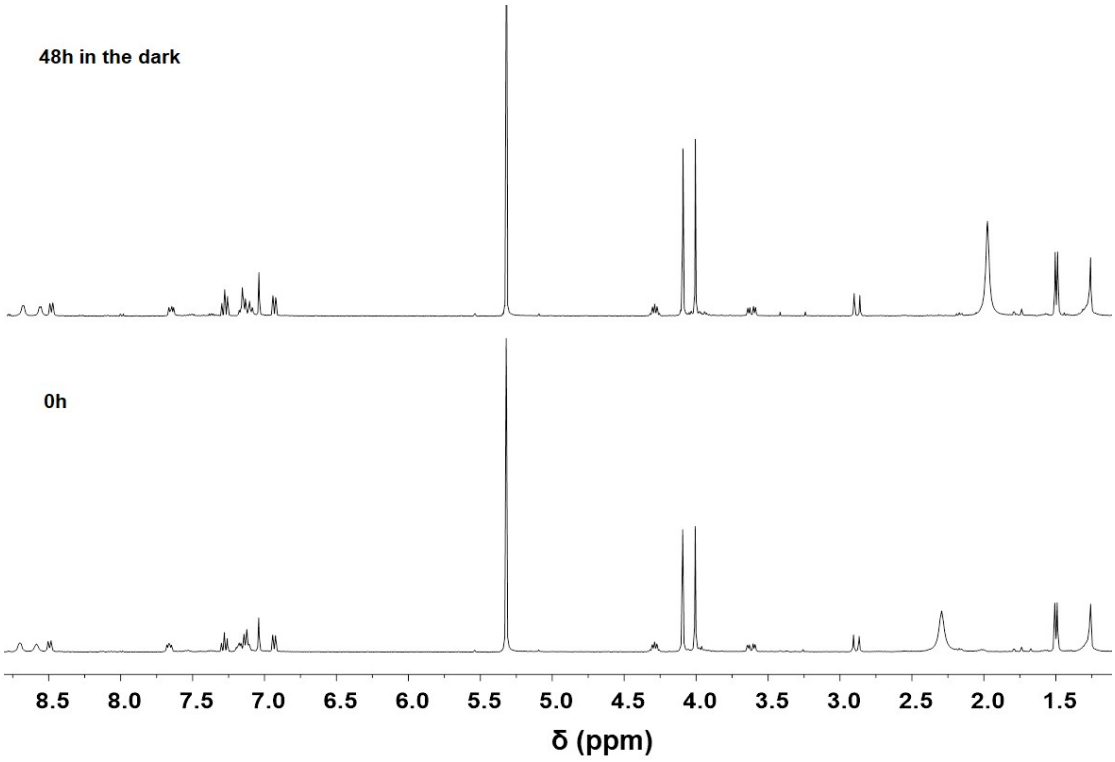


Figure S11. Stability of $\mathbf{AgL_2}$ in CD_2Cl_2 solution monitored by ^1H NMR (400 MHz) at 298 K

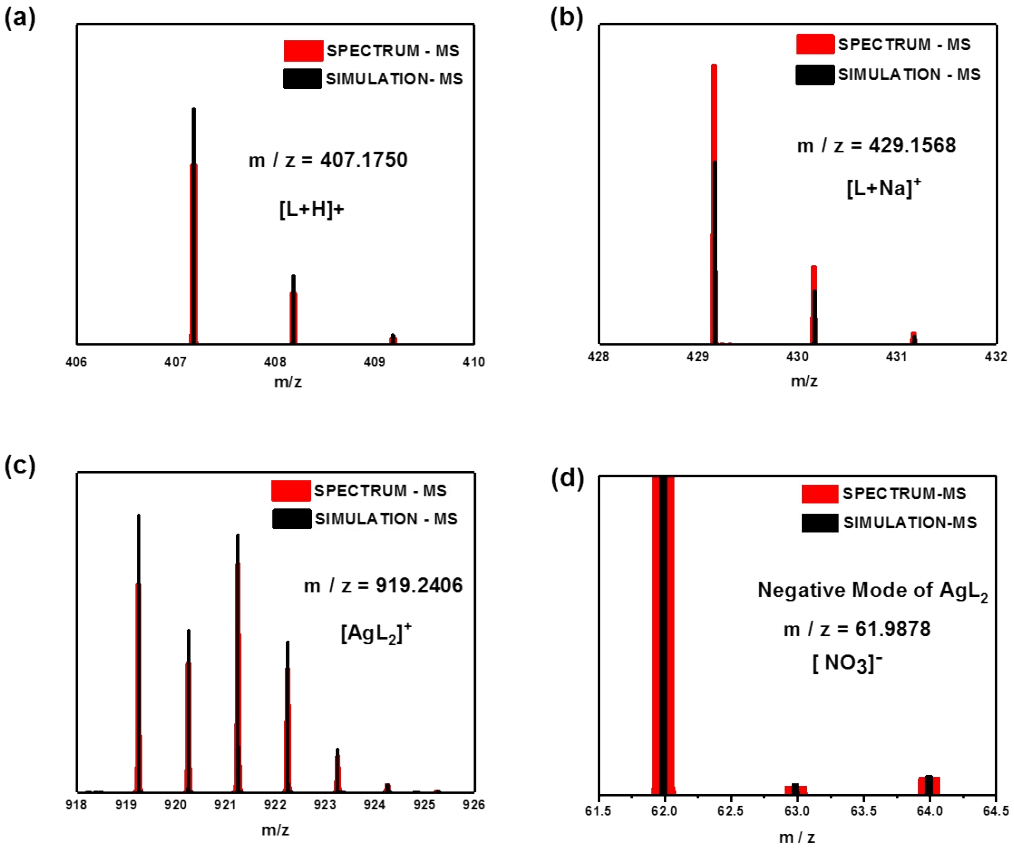


Figure S12. High resolution mass spectrum of (a, b) **L** and (c, d) $\mathbf{AgL_2}$.

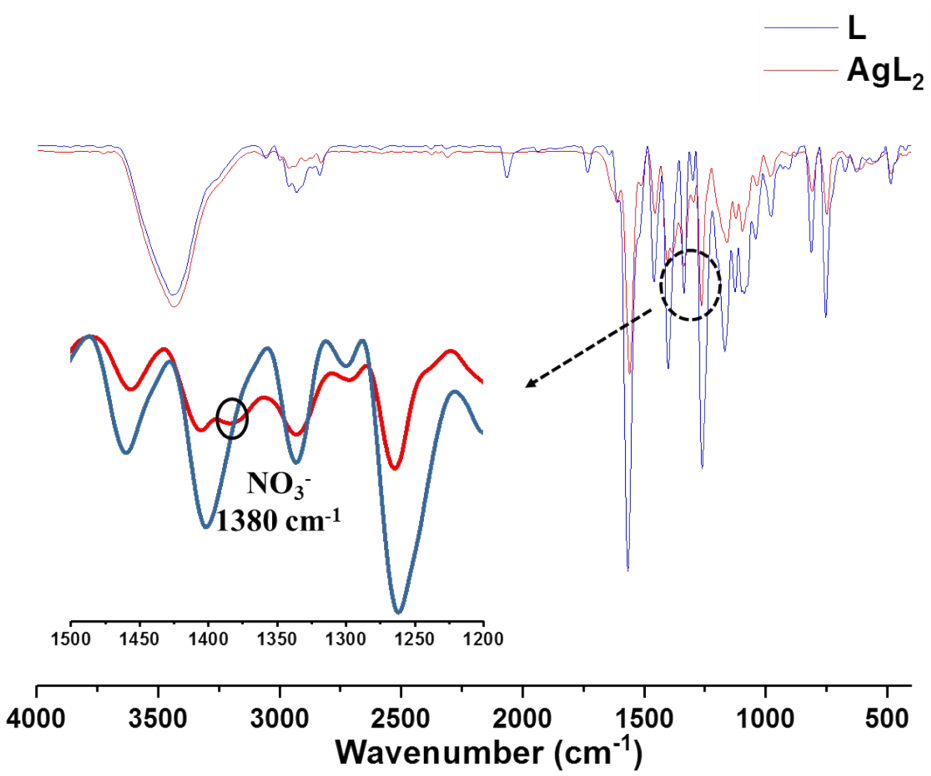


Figure S13. FT-IR spectrum of **L** and **AgL$_2$**.

6 Crystal data of L and AgL_2

Table S6. Crystal parameters of **L** and **AgL_2**

Complex	**L**	**AgL_2**
Empirical formula	$C_{54}H_{44}N_4O_4$	$C_{54}H_{44}Ag_1N_4O_4$
Formula weight	812.93	922.82
Temperature / K	293(2)	293(2)
Crystal system	triclinic	monoclinic
Space group	*P*-1	*C*2/*c*
a / Å	10.8590(2)	38.1630(11)
b / Å	11.9981(2)	17.6194(7)
c / Å	16.6267(2)	7.3988(3)
α / °	76.3770(10)	90
β / °	89.7630(10)	92.801(3)
γ / °	76.2500(10)	90
V / Å^3	2041.89(6)	4969.1(3)
Z	2	4
F(000)	856.0	1908.0
D_c./ g cm^{-3}	1.322	1.234
μ / mm^{-1}	0.665	3.622
Reflns coll.	18429	15454
Unique reflns	7281	4418
R_{int}	0.0255	0.0431
[a]R_1 [I ≥ 2σ(I)]	0.0409	0.0421
[b]wR_2 (all data)	0.1164	0.1122
GOF	1.065	1.047
CCDC	2015771	2076183

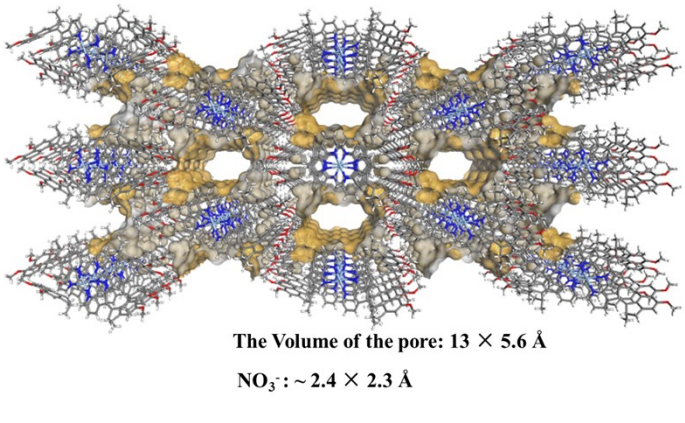


Figure S14. Perspective views of the 3D framework with 1D channels in **AgL_2**. The anion NO_3^- molecules may occupy the channels as the pore shows larger volume than NO_3^-.

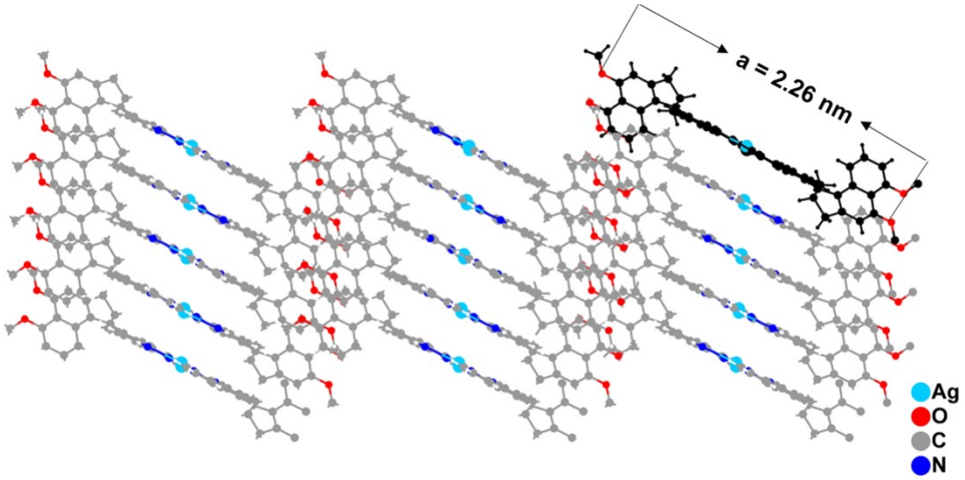


Figure S15. Packing mode of crystal structure in **AgL_2** viewed in *b* direction.

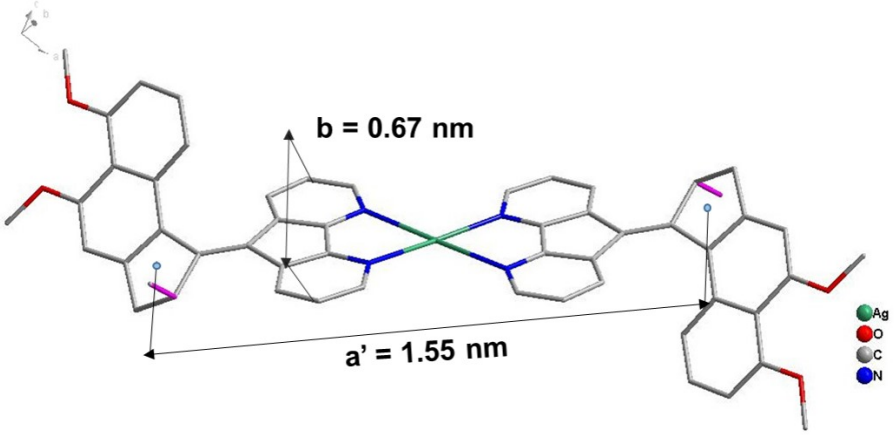


Figure S16. The width (b) and the length (a') in crystal structure of **AgL_2**.

7 DFT calculation

The DFT calculations were carried out using the Gaussian 16 program[S4]. The ground state geometries of **L** and **AgL_2** were optimized using the B3LYP functional, and the LANL2DZ basis set for Ag atom, the 6-31G(d,p) basis set for lighter atoms. In addition, the relative free energies (ΔG) of the stable and unstable isomers, as well as the transition states (TS) for THI were also calculated with the same method.

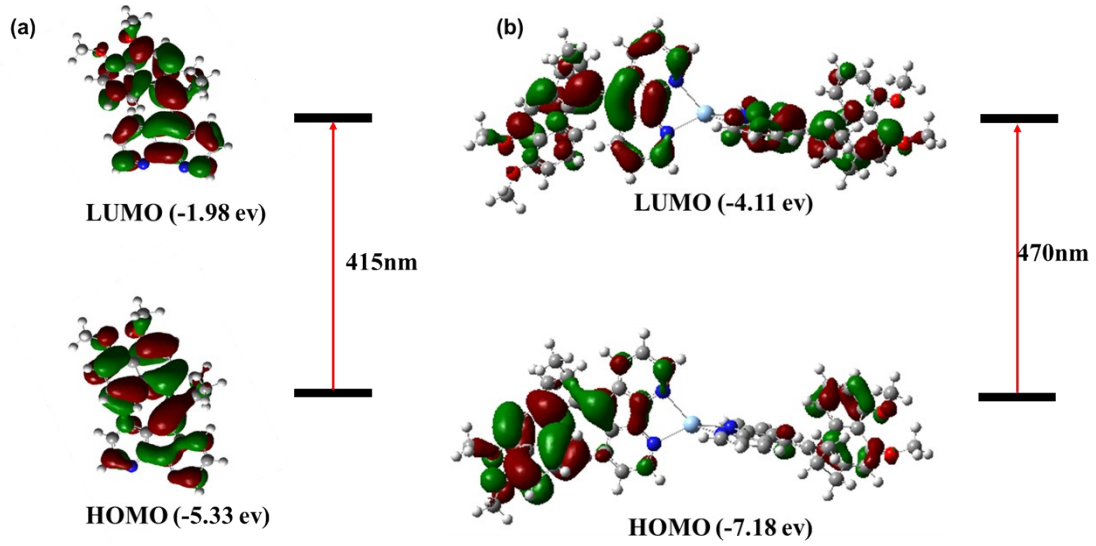


Figure S17. Structures and calculated (TD-DFT, B3LYP, 6-31G (d, p)) frontier orbitals of (a) **L**; (b) **AgL_2**.

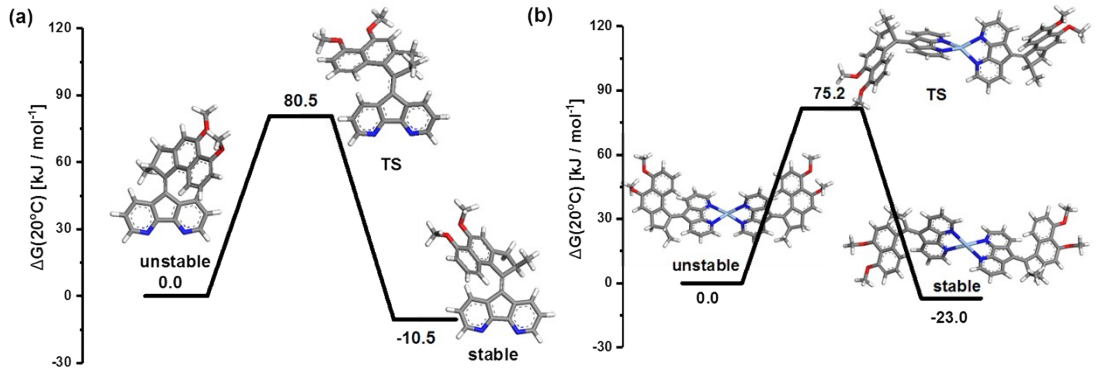
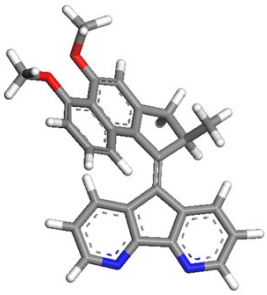


Figure S18. Energy optimization of stable, unstable, transition state (TS) on (a) **L** and (b) **AgL_2.**

Table S7. Cartesian coordinates of B3LYP optimized **stable-L**.

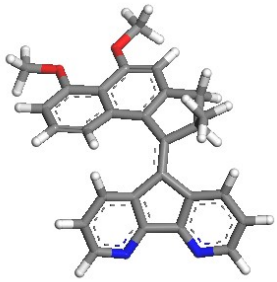


Stable-L

Atom	X	Y	Z
C	-4.01264000	-1.75491500	0.68741100
C	-3.35046800	-0.61708200	0.21848600
C	-4.13388900	0.55554700	0.04860900
N	-5.44419200	0.65593900	0.27131000
C	-6.05214100	-0.46014600	0.69358100
C	-5.38721100	-1.66942200	0.91690100
C	-1.93007900	-0.30599600	-0.08145800
C	-0.95764800	1.95118300	-1.05388500
C	-1.33793400	3.24113500	-1.42679800
C	-2.66179200	3.65399600	-1.24432400
N	-3.62839400	2.86291400	-0.76173300
C	-3.25033200	1.63208400	-0.41522000
C	-1.93003100	1.11891300	-0.49311800
C	0.89004500	1.04690400	1.26907100
C	2.50327000	-2.04359200	-1.16281600
C	3.32520700	-1.01112700	-0.74239800
C	2.81511400	0.06030300	0.06587500
C	1.13956400	-2.02487400	-0.85704300
C	0.56668600	-0.94854700	-0.18318600
C	1.40329100	0.07318200	0.37365200
C	3.62866600	1.11615700	0.61457100
C	3.07614900	2.06841900	1.45388000
C	1.71042300	2.01420700	1.79459400
C	0.10431800	-3.08145300	-1.14880900
C	-0.88308300	-1.18939600	-0.06607300
C	-1.04672700	-2.70973000	-0.16770500
C	-0.86792600	-3.43108100	1.18208500
H	-3.49756800	-2.68662300	0.88308700
H	-7.12352900	-0.38514200	0.87002400
H	-5.93977400	-2.53340000	1.27263000
H	0.05975100	1.61826100	-1.21024500
H	-0.61328400	3.92345400	-1.85996200
H	-2.96122200	4.66448100	-1.51659900

H	-0.15652400	1.00957800	1.54043900
H	2.94493900	-2.85048300	-1.73938800
H	3.69176000	2.85347000	1.87294600
H	1.30922900	2.75135700	2.48361600
H	0.48376100	-4.09768300	-0.99591400
H	-0.24577900	-3.01623600	-2.18746300
H	-2.01603000	-2.96927000	-0.59892700
H	0.12886300	-3.23997900	1.59179300
H	-0.98210400	-4.51321100	1.05643300
H	-1.59820200	-3.09516900	1.92366100
O	4.94964800	1.11135600	0.28268200
O	4.63512300	-1.05794900	-1.15196200
C	5.52645200	-1.75959200	-0.28654900
H	5.18557500	-2.78973800	-0.11942900
H	6.49392800	-1.77778700	-0.79211700
H	5.63166900	-1.24740100	0.67569300
C	5.77909800	2.15392200	0.77279800
H	6.76995100	1.96213700	0.35927900
H	5.43057600	3.13789000	0.43610500
H	5.83565900	2.14827100	1.86875800
Sum of electronic and thermal Free Energies = -1301.708442			

Table S8. Cartesian coordinates of B3LYP optimized **TS-L**



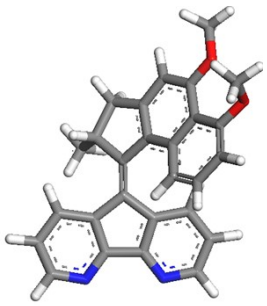
TS-L

Atom	X	Y	Z
C	-3.93786100	-1.91805700	-0.00519100
C	-3.22467700	-0.71497300	-0.06608300
C	-3.81280900	0.30581400	-0.86928100
N	-4.88528300	0.17589500	-1.64562900
C	-5.49126800	-1.01876400	-1.62282100
C	-5.07994500	-2.06580800	-0.79950200
C	-1.94003700	-0.18183000	0.51315000
C	-1.73939100	2.39132000	1.17013300
C	-2.17017700	3.66824800	0.80172800
C	-3.01192200	3.81511900	-0.30282500
N	-3.54729400	2.77504800	-0.95369900

C	-3.13384700	1.56894200	-0.56814900
C	-2.11847800	1.29711600	0.38893200
C	1.24370700	1.51755600	1.05725000
C	2.50053700	-2.31145700	-0.16239500
C	3.34153000	-1.23659700	-0.38221800
C	2.91082700	0.09060900	-0.02052700
C	1.19287100	-2.10953400	0.29424600
C	0.65246800	-0.84986600	0.55967700
C	1.57883900	0.26405600	0.51317900
C	3.76391200	1.24779200	-0.10969500
C	3.35130000	2.47479400	0.38860500
C	2.09692500	2.59298400	1.00281700
C	0.21449200	-3.22258800	0.48138400
C	-0.83045000	-0.99506400	0.70226900
C	-1.08354100	-2.50436300	0.87712900
C	-1.51556100	-2.82227200	2.32019000
H	-3.67711400	-2.71747400	0.67530600
H	-6.36341900	-1.12943500	-2.26414800
H	-5.65518100	-2.98561100	-0.75990300
H	-1.18144800	2.27242600	2.09038200
H	-1.87975000	4.53582800	1.38572300
H	-3.32182200	4.80417500	-0.63469000
H	0.30557600	1.60146500	1.56355200
H	2.82352700	-3.32194700	-0.37804400
H	3.99955000	3.33877400	0.32955300
H	1.80233200	3.54355200	1.43792600
H	0.55571500	-3.92347000	1.25424500
H	0.09677100	-3.80880100	-0.43865700
H	-1.86714300	-2.82601400	0.19410800
H	-0.72403300	-2.54775300	3.02616600
H	-1.71435700	-3.89379000	2.43721100
H	-2.41639500	-2.27017200	2.60265200
O	4.58425700	-1.38305200	-0.89770100
O	4.98326300	1.07877600	-0.68819100
C	5.85839500	2.19064500	-0.77553800
H	6.75908400	1.81844000	-1.26572800
H	5.42848400	3.00105800	-1.37781500
H	6.12143200	2.58126800	0.21580000
C	5.03241100	-2.68382700	-1.24839800
H	4.38925600	-3.14112100	-2.01024800
H	6.03527400	-2.54891600	-1.65512300
H	5.08205800	-3.34484900	-0.37424400

Sum of electronic and thermal Free Energies = -1301.673762

Table S9. Cartesian coordinates of B3LYP optimized **unstable-L**

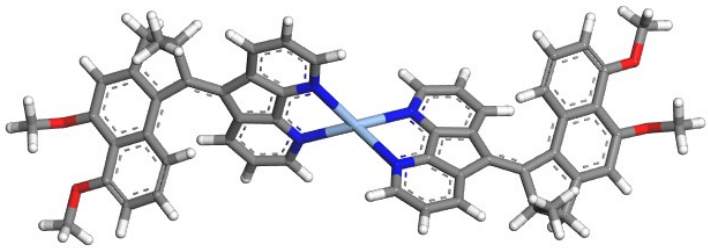


Unstable-L

Atom	X	Y	Z
C	-0.48780100	3.24426600	0.59604300
C	0.76947200	1.23748900	0.02371300
C	0.90014300	2.77422300	0.07060000
C	2.01893200	3.32597600	0.96670100
H	3.13435900	2.48576500	-1.60953900
H	6.82858300	0.28121200	-1.65690100
H	5.50213300	2.26529300	-2.35019300
H	0.02593800	-1.34939100	1.66280100
H	0.83141800	-3.49562900	2.64312300
H	3.16200500	-4.24548700	2.21660000
H	0.31513100	-1.25581000	-1.24005900
H	-3.28609300	2.95068500	0.86200800
H	-3.38165200	-3.42918700	-1.44513200
H	-0.93161300	-3.25147500	-1.94550600
H	-0.41091500	3.51617400	1.65757100
H	-0.86512800	4.13118900	0.07425600
H	1.02635100	3.16082400	-0.95161500
H	1.94588600	4.41805600	1.01675000
H	3.01933600	3.07393500	0.61803400
H	1.91378400	2.93552600	1.98414000
C	3.72664200	1.63243200	-1.29593500
C	3.20067900	0.63087200	-0.47446900
C	4.03751300	-0.48404600	-0.19833200
N	5.30206500	-0.62093700	-0.60048400
C	5.79261200	0.38230000	-1.33868300
C	5.04888400	1.50547500	-1.72118600
C	1.84600200	0.37563100	0.05575100
C	1.03710000	-1.69127400	1.47694200
C	1.49068400	-2.88774200	2.03135400
C	2.80652900	-3.30574300	1.79779600
N	3.69714400	-2.60351900	1.08666800
C	3.25038200	-1.46108100	0.56214800
C	1.92735600	-0.95860200	0.68636900

C	-0.74398400	-1.32467600	-1.03790200
C	-2.77708300	2.04586300	0.55461100
C	-3.48788300	0.88167300	0.30552100
C	-2.81797600	-0.29333900	-0.20117700
C	-1.38508400	2.05710900	0.41087200
C	-0.66061100	0.92427900	0.05219800
C	-1.38455500	-0.24953600	-0.37652200
C	-3.50187500	-1.49170800	-0.58619500
C	-2.82169000	-2.53777200	-1.18174300
C	-1.44584400	-2.44076700	-1.43838900
O	-4.84396700	-1.66929600	-0.33855200
O	-4.83088700	0.80361600	0.46823300
C	-5.52783300	1.92801900	0.98848300
H	-5.14554600	2.21484800	1.97514300
H	-5.46811400	2.78991400	0.31247400
H	-6.56751800	1.61252400	1.08026200
C	-5.71002400	-1.38140200	-1.43321400
H	-5.43524900	-1.96183300	-2.32351000
H	-6.71535100	-1.66490400	-1.11484800
H	-5.69749200	-0.31310900	-1.67873200
Sum of electronic and thermal Free Energies = -1301.704457			

Table S10. Cartesian coordinates of B3LYP optimized **stable-AgL_2**



Stable-AgL_2

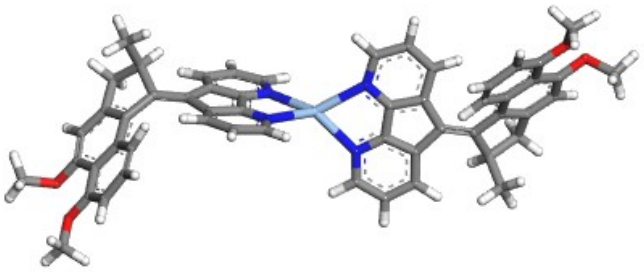
Atom	X	Y	Z
Ag	0.00063500	0.00917400	0.50608700
N	-1.61442300	1.50141300	1.59076500
C	-2.81119500	1.23857800	1.06030200
C	-1.57114200	2.48100400	2.50711800
C	-4.02851900	1.89452100	1.36379500
C	-3.06953600	0.22589000	0.05630400
C	-2.71190100	3.18680600	2.90291900
H	-0.59980700	2.70243400	2.93887400
C	-3.95776100	2.89597500	2.34017800
C	-5.11589600	1.26734900	0.57423700
N	-2.13427600	-0.53584600	-0.51784900

C	-4.45053000	0.23009400	-0.24743100
H	-2.62126900	3.96255000	3.65587800
H	-4.82988500	3.44307700	2.67416100
C	-6.43391100	1.66296700	0.54399200
C	-2.55425600	-1.36079300	-1.48991900
C	-4.85363800	-0.60023500	-1.30102600
C	-7.59805600	1.01609800	-0.06513000
C	-6.91005600	3.04807700	0.98763800
C	-3.88716400	-1.40326700	-1.91223800
H	-1.80118400	-1.99066900	-1.95371000
H	-5.87660000	-0.62566400	-1.65088600
C	-8.47631800	2.01352100	-0.49661900
C	-7.97559500	-0.36597300	-0.16245500
C	-7.97416100	3.37761900	-0.10023900
C	-7.54805800	3.04010100	2.39177300
H	-6.09174600	3.77143900	0.95687200
H	-4.16412300	-2.06492100	-2.72615600
C	-9.63804600	1.69605100	-1.20149500
C	-7.24213900	-1.38838600	0.48948100
C	-9.18290200	-0.70124800	-0.88041800
H	-8.77332300	4.02919000	0.26813700
H	-7.50397700	3.88793300	-0.95072200
H	-8.42143000	2.38128800	2.41358900
H	-7.87513300	4.04831500	2.66547200
H	-6.85230900	2.68730500	3.15866500
C	-9.97182700	0.36813400	-1.42879800
H	-10.28754200	2.46739300	-1.60312000
C	-7.63786100	-2.70239100	0.39204200
H	-6.37891400	-1.12099400	1.08507800
C	-9.54525700	-2.09412200	-0.97621000
O	-11.06141100	0.12699400	-2.21474400
C	-8.77267500	-3.06462500	-0.35543500
H	-7.07543000	-3.47780600	0.90379500
O	-10.67164000	-2.39104500	-1.66923200
C	-12.33085300	0.11735300	-1.55529100
H	-9.05106200	-4.10835400	-0.41733500
C	-11.06033400	-3.75363800	-1.80228400
H	-12.49908200	1.05422300	-1.00973900
H	-13.08086200	0.01641200	-2.34108600
H	-12.40808100	-0.73055000	-0.86685100
H	-11.96685700	-3.74248000	-2.40784800
H	-10.28952200	-4.34155300	-2.31438100
H	-11.27792900	-4.20835900	-0.82821200
N	1.61176000	-1.48577500	1.59739000

C	2.80904500	-1.22763100	1.06584200
C	1.56627500	-2.46245000	2.51670500
C	4.02480600	-1.88565800	1.37102000
C	3.06968900	-0.21860300	0.05867000
C	2.70535000	-3.16996500	2.91437300
H	0.59450100	-2.68010100	2.94942300
C	3.95179400	-2.88398100	2.35046100
C	5.11354700	-1.26356000	0.57930000
N	2.13617900	0.54371500	-0.51768700
C	4.45059000	-0.22709100	-0.24532700
H	2.61294100	-3.94318400	3.66971300
H	4.82262500	-3.43227400	2.68586900
C	6.43056700	-1.66253900	0.54991800
C	2.55797900	1.36473200	-1.49231300
C	4.85554700	0.59916900	-1.30142400
C	7.59620100	-1.02041200	-0.06139100
C	6.90331000	-3.04752200	0.99754500
C	3.89093600	1.40272500	-1.91488900
H	1.80638000	1.99498700	-1.95795500
H	5.87851800	0.62110200	-1.65149300
C	8.47184900	-2.02133000	-0.49009800
C	7.97720500	0.36040500	-0.16289600
C	7.96633800	-3.38297700	-0.08958500
C	7.54165400	-3.03702600	2.40150800
H	6.08317100	-3.76890000	0.96908200
H	4.16936000	2.06130700	-2.73079400
C	9.63430000	-1.70887100	-1.19601500
C	7.24645100	1.38659900	0.48613700
C	9.18523200	0.69051600	-0.88205800
H	8.76393200	-4.03547300	0.28054200
H	7.49466300	-3.89461300	-0.93844700
H	8.41673400	-2.38041600	2.42117600
H	7.86617900	-4.04526800	2.67812100
H	6.84699400	-2.68015500	3.16750100
C	9.97145800	-0.38248300	-1.42723300
H	10.28186100	-2.48301000	-1.59537300
C	7.64538500	2.69932300	0.38463500
H	6.38272800	1.12313800	1.08276000
C	9.55090300	2.08221500	-0.98226600
O	11.06174300	-0.14656300	-2.21380500
C	8.78086400	3.05649800	-0.36426600
H	7.08500700	3.47766300	0.89419300
O	10.67773400	2.37427900	-1.67662400
C	12.33101400	-0.13712100	-1.55400000

H	9.06175900	4.09935400	-0.42948100
C	11.06960700	3.73552400	-1.81408800
H	12.49727600	-1.07251100	-1.00531100
H	13.08143500	-0.04021600	-2.33990800
H	12.40968200	0.71290000	-0.86834900
H	11.97586700	3.72031700	-2.41995800
H	10.29999000	4.32365700	-2.32772900
H	11.28865400	4.19277200	-0.84152600
Sum of electronic and thermal Free Energies = -2749.043464			

Table S11. Cartesian coordinates of B3LYP optimized **TS-AgL$_2$**



TS-AgL$_2$

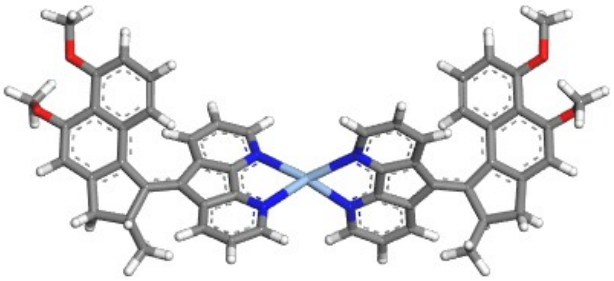
Atom	X	Y	Z
Ag	0.01720000	0.10504300	-0.42819400
N	1.46999000	-1.87474300	-0.50343600
C	2.73109700	-1.43735600	-0.47698700
C	1.30239300	-3.20281600	-0.59936900
C	3.89980200	-2.23306100	-0.54767900
C	3.12430800	-0.04569200	-0.38193900
C	2.38104800	-4.09145200	-0.65595700
H	0.27898700	-3.56459700	-0.62641500
C	3.69510800	-3.61644400	-0.62297800
C	5.08480600	-1.34636000	-0.45173300
N	2.27754300	0.98748500	-0.37195100
C	4.53630000	0.02694100	-0.36566200
H	2.18779800	-5.15688900	-0.72271500
H	4.51413300	-4.32357500	-0.65063700
C	6.40221300	-1.73364600	-0.54434400
C	2.83193400	2.20997900	-0.36449500
C	5.08906900	1.31310900	-0.41195500
C	7.62831500	-0.97001300	-0.30184400
C	6.85125900	-3.05802600	-1.16594600
C	4.21663600	2.40461500	-0.40207500

H	2.14957400	3.05435700	-0.34545800
H	6.15691100	1.47606300	-0.46330100
C	8.61597600	-1.44176200	-1.17027100
C	7.95370500	0.01680100	0.68923000
C	8.11225700	-2.61771400	-1.96621700
C	7.21729200	-4.12066400	-0.10983900
H	6.08699900	-3.45311200	-1.83940800
H	4.60888700	3.41574600	-0.42881900
C	9.87235100	-0.83732100	-1.23010100
C	7.06605900	0.33328000	1.74769200
C	9.25648500	0.63803700	0.64096400
H	8.85848500	-3.41368600	-2.05838000
H	7.83148800	-2.31523600	-2.98331400
H	8.03989200	-3.76898200	0.52020600
H	7.53465400	-5.04749900	-0.59836100
H	6.37587500	-4.35333100	0.54937000
C	10.18133000	0.20948000	-0.37275600
H	10.61955300	-1.15042600	-1.95244700
C	7.41229700	1.27130100	2.69256400
H	6.12057600	-0.18880300	1.81750100
C	9.56611200	1.63277900	1.63855700
O	11.38544500	0.82645300	-0.55384200
C	8.64820700	1.93971100	2.63216700
H	6.72981900	1.49972000	3.50591500
O	10.78673200	2.21787000	1.56652100
C	12.50894900	0.23134200	0.10176900
H	8.88496500	2.67741000	3.38744800
C	11.13032600	3.21591800	2.52103000
H	12.61628900	-0.82377100	-0.17912800
H	13.38606500	0.78632700	-0.23417500
H	12.41825500	0.31705500	1.18956800
H	12.13292200	3.54802300	2.25058000
H	10.44160800	4.06775100	2.47506100
H	11.14247600	2.81221600	3.54076000
N	-1.82393300	0.66890700	-1.91261200
C	-2.90006200	0.92988000	-1.16043800
C	-1.97763100	0.77307600	-3.23746600
C	-4.17880400	1.32899100	-1.61826600
C	-2.94431000	0.80228900	0.27337600
C	-3.21334800	1.08502800	-3.81684700
H	-1.10283500	0.57970800	-3.85087100
C	-4.32656300	1.33962100	-3.01716900
C	-5.11003600	1.41089600	-0.45172300
N	-1.88015100	0.51991500	1.03333800

C	-4.26348900	1.08550400	0.72200800
H	-3.30288400	1.11231800	-4.89768900
H	-5.27649400	1.52235600	-3.50266800
C	-6.47363200	1.65448200	-0.65019200
C	-2.06409000	0.54107200	2.35886000
C	-4.38383000	1.20311000	2.11538400
C	-7.73042400	1.00342100	-0.23133700
C	-6.89484200	2.63563300	-1.75384400
C	-3.28895200	0.90535800	2.92609400
H	-1.20739600	0.29372000	2.97846400
H	-5.28915800	1.54082700	2.59112200
C	-8.57896500	1.02505400	-1.35257400
C	-8.15540500	0.24708900	0.92055200
C	-8.09392300	1.95541100	-2.42972700
C	-7.28594600	3.97286700	-1.08012700
H	-6.08933400	2.86571600	-2.44420600
H	-3.37831700	0.97289200	4.00515000
C	-9.68031300	0.17243700	-1.45735700
C	-7.59785400	0.47054200	2.19452000
C	-9.25635600	-0.67825300	0.79894600
H	-8.87259600	2.65976700	-2.74304900
H	-7.79479300	1.39323200	-3.32427100
H	-8.13824800	3.84605900	-0.40597000
H	-7.55925500	4.70430100	-1.84743400
H	-6.45046300	4.38100900	-0.50408700
C	-9.98479000	-0.71383000	-0.43892200
H	-10.27602700	0.14292500	-2.36428100
C	-7.98655700	-0.26913700	3.28855200
H	-6.92529200	1.30264600	2.30773500
C	-9.60386900	-1.47194900	1.95030900
O	-10.97889500	-1.61790800	-0.67105400
C	-8.95873400	-1.27365600	3.16366000
H	-7.55245500	-0.07083600	4.26412100
O	-10.59602700	-2.38135200	1.79241700
C	-12.31182300	-1.18554500	-0.38092800
H	-9.23194500	-1.85740300	4.03263400
C	-10.96484800	-3.19897400	2.89778100
H	-12.55111700	-0.25954500	-0.91823000
H	-12.97131100	-1.98420600	-0.72329100
H	-12.44989500	-1.03523400	0.69476900
H	-11.75095900	-3.85671300	2.52635900
H	-10.12014000	-3.80445100	3.24666700
H	-11.35328100	-2.60062400	3.73085000

Sum of electronic and thermal Free Energies = -2749.006061

Table **S12**. Cartesian coordinates of B3LYP optimized **unstable-AgL_2**



Unstable-AgL_2

Atom	X	Y	Z
Ag	0.00008800	-1.03089100	0.00063200
N	1.78903200	-2.18130900	-1.24906100
C	2.94294700	-1.69439700	-0.78396500
C	1.88121700	-3.13092400	-2.19172900
C	4.24275700	-2.09860800	-1.17591600
C	3.06976900	-0.63705000	0.19627100
C	3.11151400	-3.57759200	-2.69172000
H	0.94720400	-3.53807100	-2.56711800
C	4.30837300	-3.05793800	-2.19520600
C	5.23552300	-1.26174100	-0.47421300
N	2.05255800	-0.06247000	0.84569200
C	4.44500900	-0.34989500	0.37422300
H	3.12402800	-4.33029900	-3.47292100
H	5.25340300	-3.39887200	-2.60359100
C	6.61564100	-1.37977600	-0.54482700
C	2.37811800	0.86154600	1.76269100
C	4.75970100	0.58650200	1.36798100
C	7.63309900	-0.36701700	-0.30737800
C	7.33085400	-2.72164100	-0.79308300
C	3.70675200	1.19439500	2.05452600
H	1.55583700	1.33880600	2.28704100
H	5.78473600	0.83840500	1.60981300
C	8.87277200	-0.98766600	-0.11320900
C	7.57813800	1.07490100	-0.40088100
C	8.78365800	-2.47154000	-0.29870800
C	6.72135100	-3.93656000	-0.07448500
H	7.36265900	-2.91481700	-1.87519100
H	3.90989000	1.93139800	2.82436600
C	10.01549500	-0.25551200	0.20587000
C	6.45499100	1.75071100	-0.93358200
C	8.74817900	1.83834400	-0.03184100

H	8.95495200	-2.99906800	0.64850400
H	9.54408500	-2.83639800	-0.99783500
H	6.67397100	-3.75335700	1.00389500
H	7.35406000	-4.81516200	-0.23731200
H	5.71574700	-4.18358900	-0.41384900
C	9.95316100	1.12637600	0.30466600
H	10.97080900	-0.73849500	0.38325000
C	6.44768600	3.12322400	-1.05057900
H	5.61161400	1.17647900	-1.28908300
C	8.67831500	3.27490900	-0.12524500
O	11.11595000	1.76175500	0.62444200
C	7.54105800	3.89339900	-0.62450300
H	5.58629000	3.62388600	-1.48276200
O	9.76735700	3.97168800	0.28066700
C	11.28156300	2.11920300	2.00078100
H	7.49556300	4.97100600	-0.71061000
C	9.78808400	5.38488600	0.11033700
H	11.22806300	1.22969800	2.64086200
H	12.27460100	2.56367900	2.07973400
H	10.53034000	2.85051200	2.31380200
H	10.76829700	5.70854000	0.46099900
H	9.66907300	5.66134500	-0.94358400
H	9.00871100	5.87469300	0.70666400
N	-1.78904000	-2.18122900	1.24915900
C	-2.94290700	-1.69427100	0.78402200
C	-1.88127100	-3.13099700	2.19166000
C	-4.24273200	-2.09855900	1.17580800
C	-3.06969400	-0.63677600	-0.19608400
C	-3.11160800	-3.57776700	2.69148700
H	-0.94729200	-3.53820600	2.56705600
C	-4.30842400	-3.05803400	2.19496300
C	-5.23549700	-1.26163800	0.47419100
N	-2.05249100	-0.06213400	-0.84540000
C	-4.44494700	-0.34962900	-0.37403300
H	-3.12415600	-4.33058300	3.47258200
H	-5.25350400	-3.39897800	2.60322300
C	-6.61561000	-1.37979800	0.54459900
C	-2.37803900	0.86197700	-1.76232200
C	-4.75961900	0.58688400	-1.36767000
C	-7.63310100	-0.36707100	0.30710600
C	-7.33077900	-2.72173600	0.79255700
C	-3.70664700	1.19486200	-2.05413700
H	-1.55572600	1.33927700	-2.28659700
H	-5.78463500	0.83884500	-1.60951700

C	-8.87269400	-0.98778000	0.11261900
C	-7.57825200	1.07483700	0.40080000
C	-8.78351000	-2.47167400	0.29794000
C	-6.72105300	-3.93652200	0.07392000
H	-7.36277500	-2.91505600	1.87463300
H	-3.90981300	1.93192800	-2.82390800
C	-10.01541300	-0.25566100	-0.20655800
C	-6.45525000	1.75066500	0.93379200
C	-8.74827600	1.83824600	0.03164000
H	-8.95460100	-2.99910300	-0.64936200
H	-9.54403400	-2.83666700	0.99689300
H	-6.67348900	-3.75318400	-1.00442900
H	-7.35372600	-4.81519200	0.23652400
H	-5.71549200	-4.18351900	0.41343500
C	-9.95315700	1.12624500	-0.30514400
H	-10.97066900	-0.73868200	-0.38414800
C	-6.44806700	3.12316100	1.05096100
H	-5.61189200	1.17644800	1.28936500
C	-8.67851300	3.27480800	0.12518100
O	-11.11593800	1.76161200	-0.62499000
C	-7.54140500	3.89331500	0.62475000
H	-5.58679600	3.62383400	1.48338200
O	-9.76750300	3.97155400	-0.28093200
C	-11.28142600	2.11911400	-2.00132600
H	-7.49599200	4.97091500	0.71098000
C	-9.78837700	5.38473200	-0.11045800
H	-11.22773700	1.22965600	-2.64145700
H	-12.27450700	2.56347600	-2.08038100
H	-10.53024900	2.85053300	-2.31421000
H	-10.76853400	5.70834900	-0.46131200
H	-9.66962900	5.66108900	0.94352000
H	-9.00890500	5.87466200	-0.70655400

Sum of electronic and thermal Free Energies = -2749.034720

Reference

S1. P. J. Davis, L. Harrisa, A. Karim, A. L.Thompson, M. Gilpin, M. G. Moloney, M. J. Pound and C. Thompson. *Tetrahedron Letters.* 2011, **52***,* 1553-1556.

S2. C. Li, H. Yan, L. X. Zhao, G. F. Zhang, Z. Hu, Z. L. Huang and M. Q. Zhu. *Nat. Commun*., 2014, **5**, 5709.

S3. S. Wiedbrauk, B. Maerz, E. Samoylova, A. Reiner, F. Trommer, P. Mayer, W. Zinth and H. Dube. Twisted hemithioindigo photoswitches: Solvent polarity determines the

type of light-induced rotations. *J. Am. Chem. Soc.,* 2016, **138**, 12219-12227.

S4. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox,Gaussian 16, Revision A.03, Gaussian, Inc., Wallingford CT, 2016.