Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

Photochromism of Aminobenzopyrano-Xanthene with Different Fluorescent Behavior in Solution and Crystal State

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1. Materials and General Methods

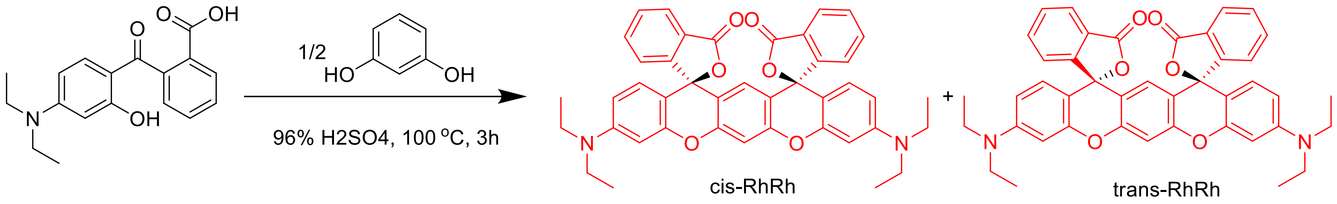
All the solvents and reactants were purchased from commercialized companies and used as received without further purification except for specifying otherwise.

^{1}H NMR was recorded on the 400 MHz (Bruker ARX400) and ^{13}C NMR spectra were recorded on the Bruker 125 MHz spectrometer at room temperature with $CDCl_3$ as the solvent and tetramethylsilane (TMS) as the internal standard. ESI high resolution mass-spectra (HRMS) were acquired on a Bruker Apex IV FTMS mass spectrometer. UV-Vis spectra were acquired on the Hitachi U-4100 UV-vis spectrophotometer. Steady fluorescence spectra were performed on the Hitachi F-7000 or Edinburgh Instruments FLS920 fluorescence spectrophotometer. Single crystal X-ray diffraction data were collected with a NONIUS KappaCCD diffractometer with graphite monochromator and Mo Kα radiation [λ (MoKα) = 0.71073 Å]. Structures were solved by direct methods with SHELXS-97 and refined against F2 with SHELXS-97.

Photochromism of single crystals: The single crystal was irradiated under 375 nm laser. The laser was directed into the microscope and focused on the sample by a 50×/0.75 NA objective and the power was 2.62 mW. The fluorescence spectra were measured using a fluorescence microscope (IX71, Olympus 20×, numerical aperture = 0.4) equipped with a spectrometer (Horiba Jobin Yvon iHR320), and the light source of which was a mercury lamp with an excitation wavelength of 365 nm. UV−visible absorption spectra were measured with an optical fiber spectrometer (Ocean Optics, QE65 Pro) using a deuterium−halogen light source.

Photochromism in solution: The solution was irradiated under 365 nm LED light (OMRON ZUV-C20H) with the power of 70 mW. Ultraviolet−visible (UV−vis) spectra of the cis/trans-RhRh solutions in different solvents were recorded by a UV−vis spectrometer (Ocean Optics, USB4000), while the fluorescence spectra were obtained on a Shimadzu 5301PC fluorescence spectrophotometer.

1. Synthesis of targeted molecule cis/trans-RhRh



Scheme S1. The synthetic route to cis/trans-RhRh.

2-(4-(diethylamino)-2-hydroxybenzoyl)benzoic acid (2.5 g, 0.8 mmol) and resorcinol (0.44 g, 0.4 mmol) were both placed in 150 ml round-bottomed flask. Concentrated sulfric acid (10 ml) was then added and the solution was kept stirring at 100 °C for 3h. After the mixture was cooled down to room temperature and poured into ice water (100 mL) with vigorous stirring, the pH of the mixture was adjusted to ~7. The mixture was extracted with dichloromethane (20 mL) three times. The organic layers were dried over anhydrous sodium sulfate and evaporated to give the crude product of the mixture of cis-RhRh and trans-RhRh. The purification and separation of the stereoisomer were achieved by silica column chromatography eluting with dichloromethane and methanol (300:1) to give the pure form of cis-RhRh and trans-RhRh as a pink solid in the ratio of about 1:1.

cis-RhRh:

^{1}H NMR (400 MHz, $CDCl_3$), δ/ppm: 7.81 (dd, *J* = 5.8, 2.7 Hz, 2H), 7.48 – 7.39 (m, 4H), 7.13 (s, 1H), 6.99 – 6.83 (m, 2H), 6.47 (dd, *J* = 15.7, 10.6 Hz, 4H), 6.32 (d, *J* = 8.6 Hz, 2H), 5.98 (s, 1H), 3.35 (q, *J* = 7.0 Hz, 8H), 1.16 (t, *J* = 7.0 Hz, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ/ppm: 168.93, 153.36, 153.22, 152.23, 149.81, 134.20, 129.36, 128.76, 128.60, 127.38, 124.97, 123.53, 116.44, 108.65, 105.30, 104.39, 97.93, 83.34, 44.66, 12.60.

HR-ESI-MS Calcd. For $C_{42}H_{37}N_2O_6$ $[M+H]^+$: 665.26461. Found: 665.26473.

trans-RhRh:

^{1}H NMR (400 MHz, $CDCl_3$), δ/ppm: δ 7.78 (d, *J* = 7.6 Hz, 2H), 7.61 (t, *J* = 7.2 Hz, 2H), 7.51 (t, *J* = 7.4 Hz, 2H), 7.17 – 7.05 (m, 3H), 6.49 (d, *J* = 8.9 Hz, 4H), 6.33 (d, *J* = 8.6 Hz, 2H), 6.04 (s, 1H), 3.35 (q, *J* = 7.0 Hz, 8H), 1.17 (t, *J* = 7.0 Hz, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ/ppm: 168.93, 153.36, 153.22, 152.23, 149.81, 134.20, 129.36, 128.76, 128.60, 127.38, 124.97, 123.53, 116.44, 108.65, 105.30, 104.39, 97.93, 83.34, 44.66, 12.60.

HR-ESI-MS Calcd. For $C_{42}H_{37}N_2O_6$ $[M+H]^+$: 665.26461. Found:665.26540.

2. NMR spectra and HR-MS of An=RhB-1 and An=RhB-2

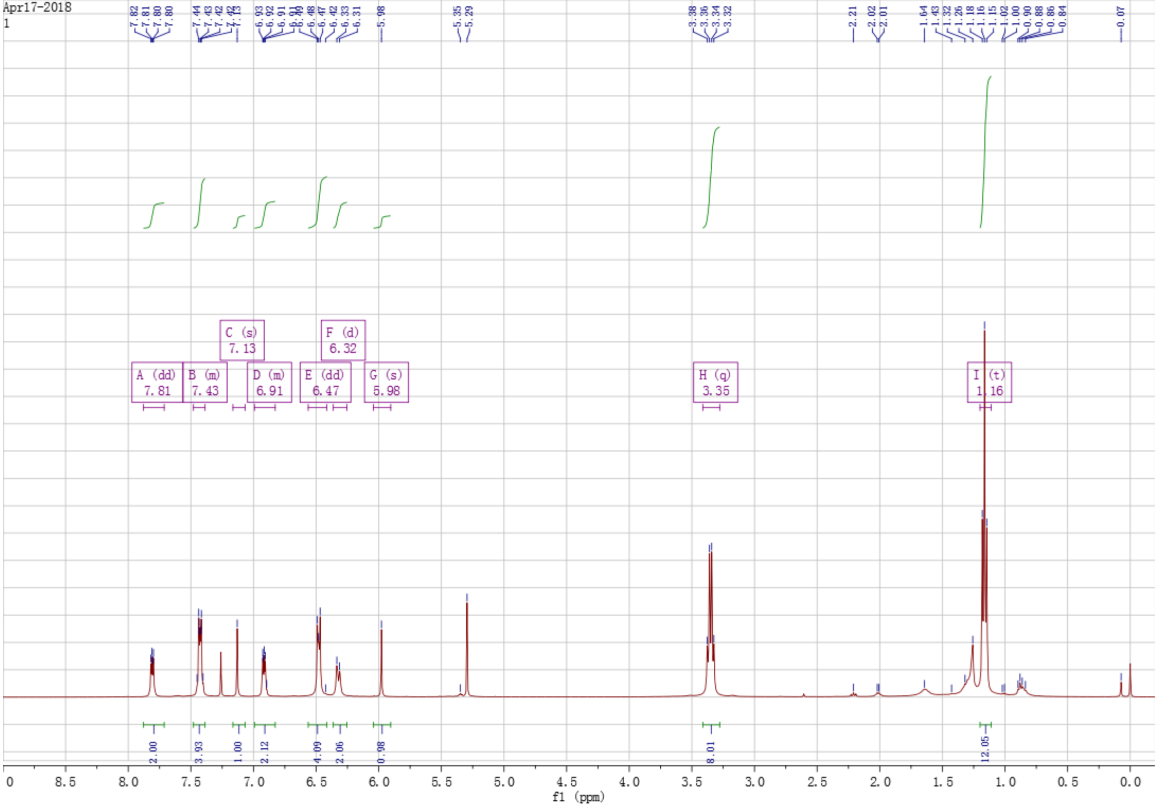


Figure S1. ^{1}H NMR spectrum of **cis-RhRh** in CDCl$_3$.

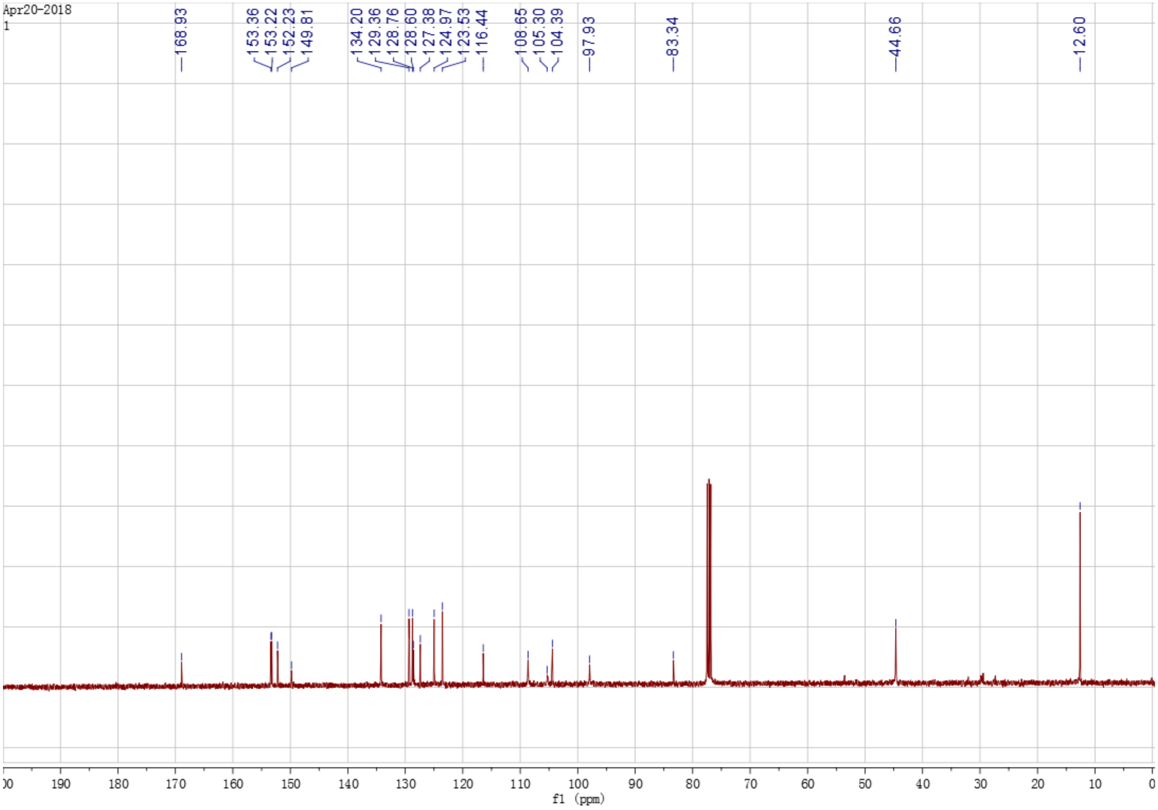
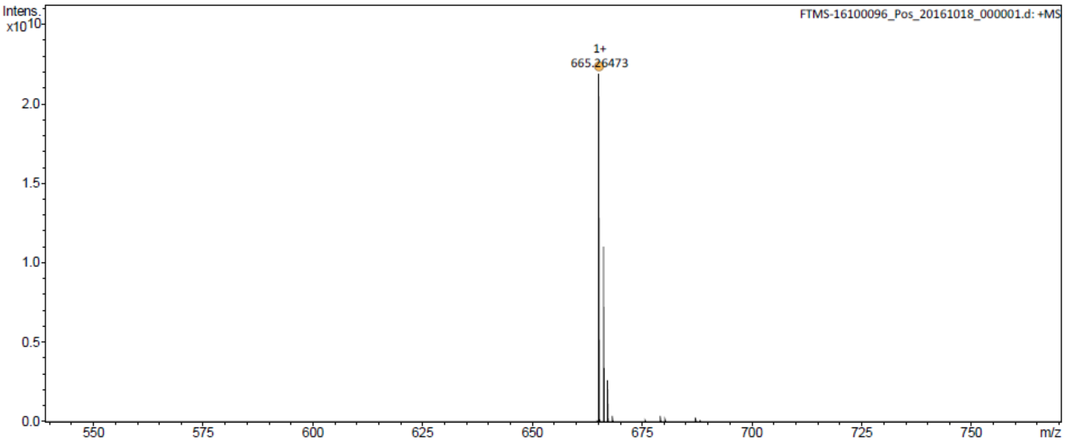


Figure S2. ^{13}C NMR spectrum of **cis-RhRh** in CDCl$_3$.



Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
665.264732	1	C42H37N2O6	100.00	665.264613	-0.2	0.2	16.1	26.0	even	ok

Figure S3. HR-MS spectrum of **cis-RhRh**.

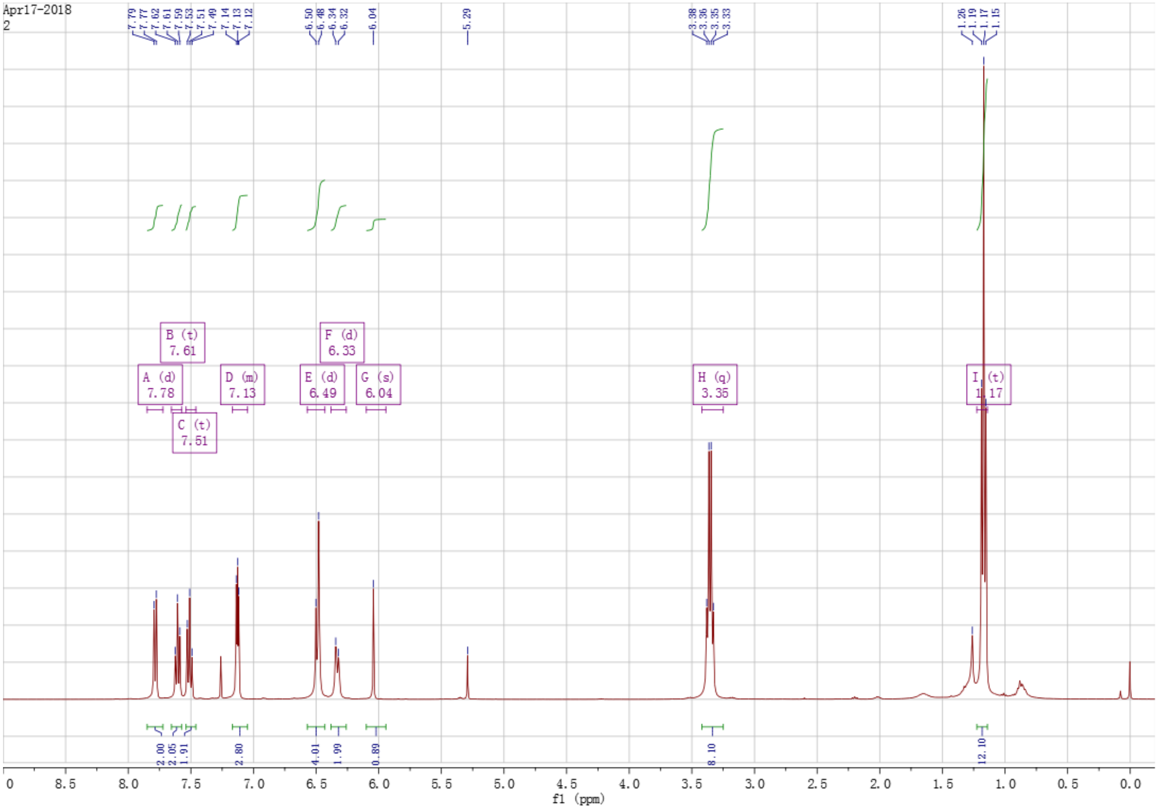


Figure S4. ^{1}H NMR spectrum of **trans-RhRh** in $CDCl_3$.

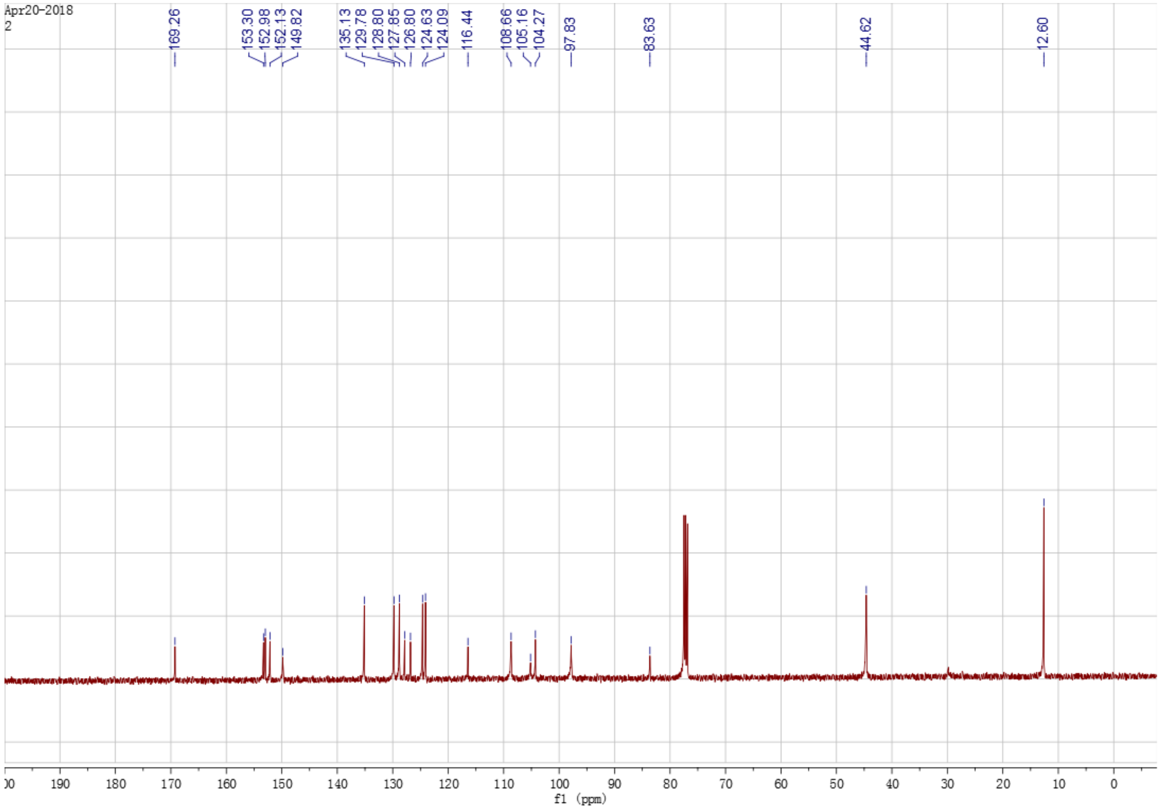
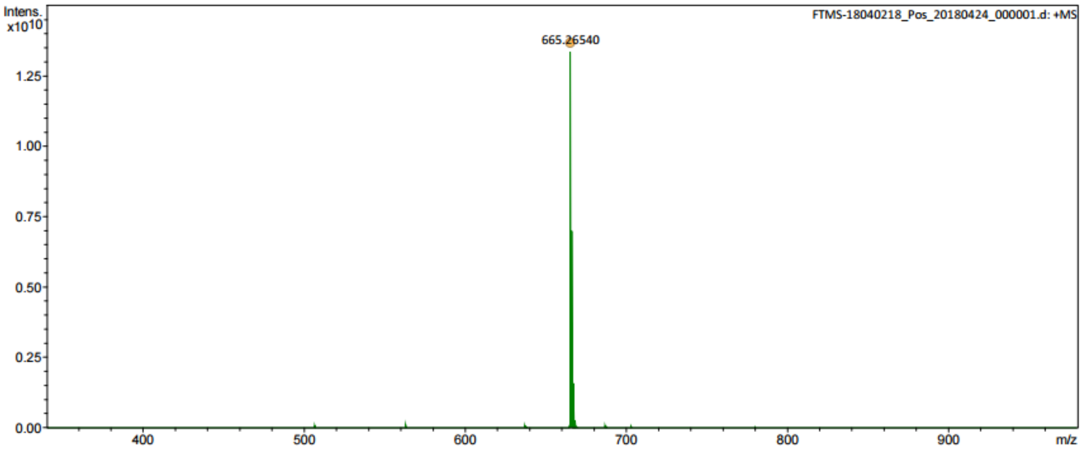


Figure S5. ^{13}C NMR spectrum of **trans-RhRh** in $CDCl_3$.



Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e¯ Conf	N-Rule
665.265401	1	C42H37N2O6	100.00	665.264613	-1.2	-4.2	25.6	26.0	even	ok

Figure S6. HR-MS spectrum of **trans-RhRh**.

3. Data table of cis-RhRh and trans-RhRh single crystal

Table S1. Detailed data of cis-RhRh and trans-RhRh single crystal.

Identification code	**cis-RhRh**	**trans-RhRh**
CCDC Number	1834084	1834085
Empirical formula	CH_2Cl_2, $C_{42}H_{36}N_2O_6$	$C_{42}H_{36}N_2O_6$
Formula weight	749.65	664.73
Temperature	106 K	107 K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	monoclinic	orthorhombic
Space group	P 1 21/n 1	P b c n
Unit cell dimensions	a = 15.728(2) Å, α= 90.00°.	a = 14.6100(12) Å, α= 90.00°.
	b = 15.8995(14) Å, β= 112.226(17).	b = 19.4506(11) Å, β= 90.00°.
	c = 15.969(3) Å, γ = 90.00°.	c = 12.1904(11) Å, γ = 90.00°.
Volume	3696.7(8) $Å^3$	3464.2(5) $Å^3$
Z	4	4
Density (calculated)	1.347 Mg/m^3	1.275 Mg/m^3
Absorption coefficient	0.228 mm^{-1}	0.085 mm^{-1}
F(000)	1568	1400
Crystal size	0.40 x 0.30 x 0.25 mm^3	0.25 x 0.23 x 0.14 mm^3
Theta range for data collection	2.91 to 29.50°.	2.97 to 29.17°.
Index ranges	-19<=h<=19, -19<=k<=19, -19<=l<=19	-11<=h<=18, -23<=k<=21, -14<=l<=15
Reflections collected	21001	11356
Independent reflections	7261 [R(int) = 0.0527]	3396 [R(int) = 0.0645]
Final R indices [I>2sigma(I)]	R1 =0.0655, wR2 = 0.1595	R1 = 0.0952, wR2 = 0.2170
R indices (all data)	R1 = 0.0910, wR2 = 0.1755	R1 = 0.1465, wR2 = 0.2502

4. Photophysical property of cis/trans-RhRh in DCM solution

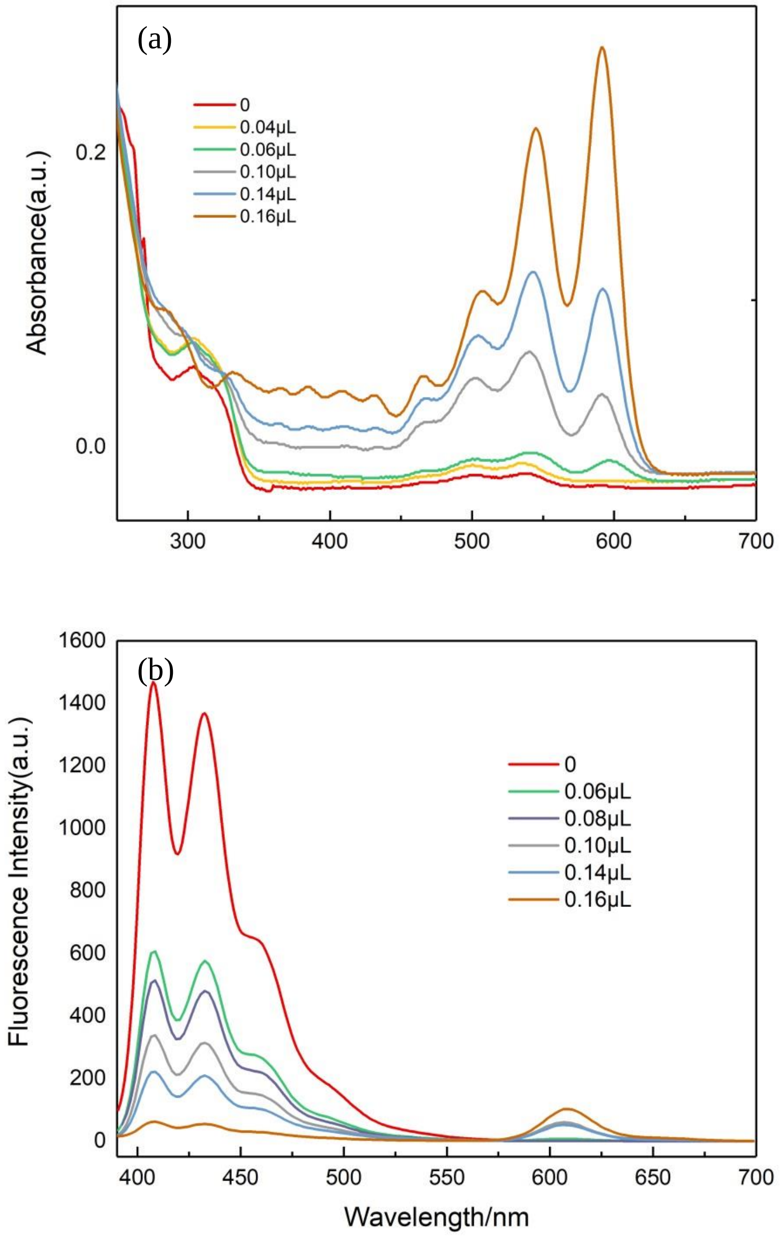


Figure S7. (a) Absorption spectra and (b) fluorescence spectra of cis-RhRh in DCM solution (6.7 μM) with the addition of different volume of TFA.

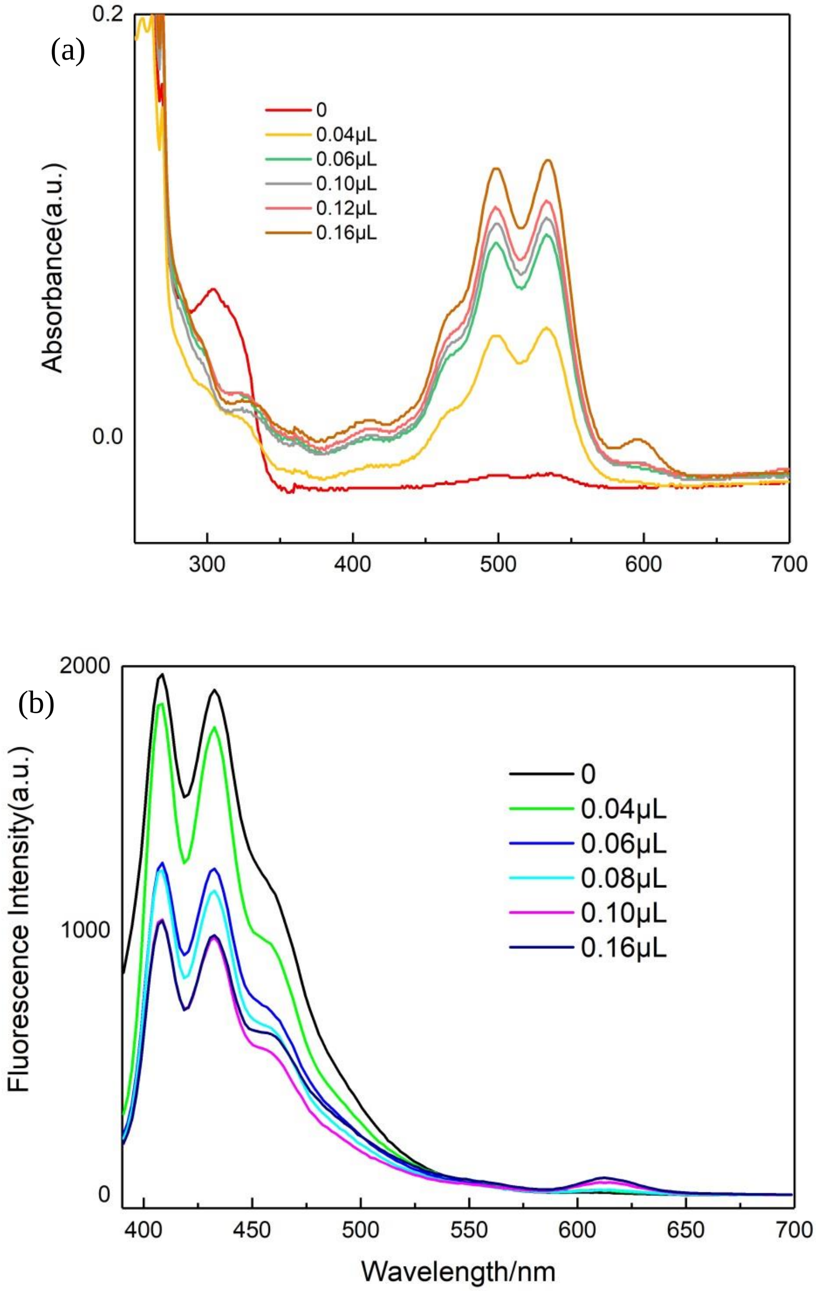


Figure S8. (a) Absorption spectra and (b) fluorescence spectra of trans-RhRh in DCM solution (6.7 μ M) with the addition of different volume of TFA.

5. The generation process of new species by adding TFA

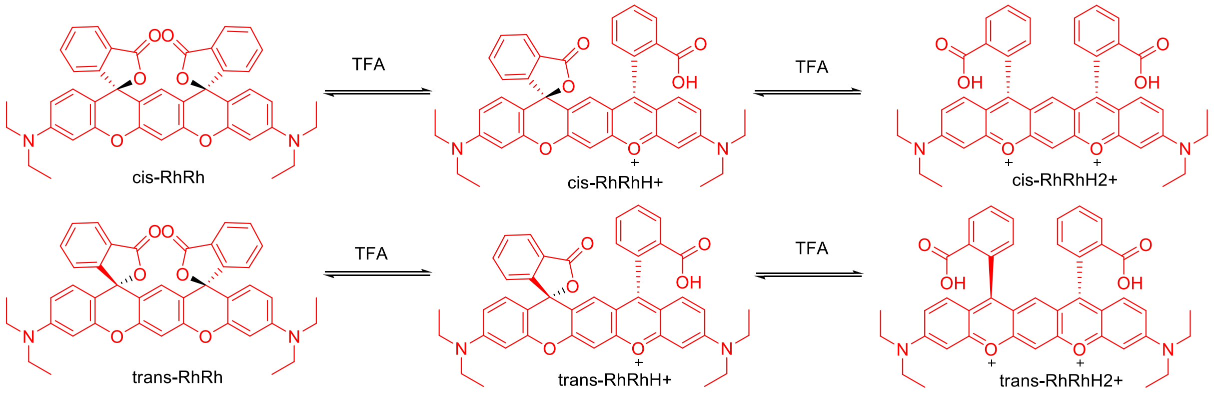


Figure S9. The generation process of new species by adding TFA.

6. Photochromic reversibility of cis/trans-RhRh

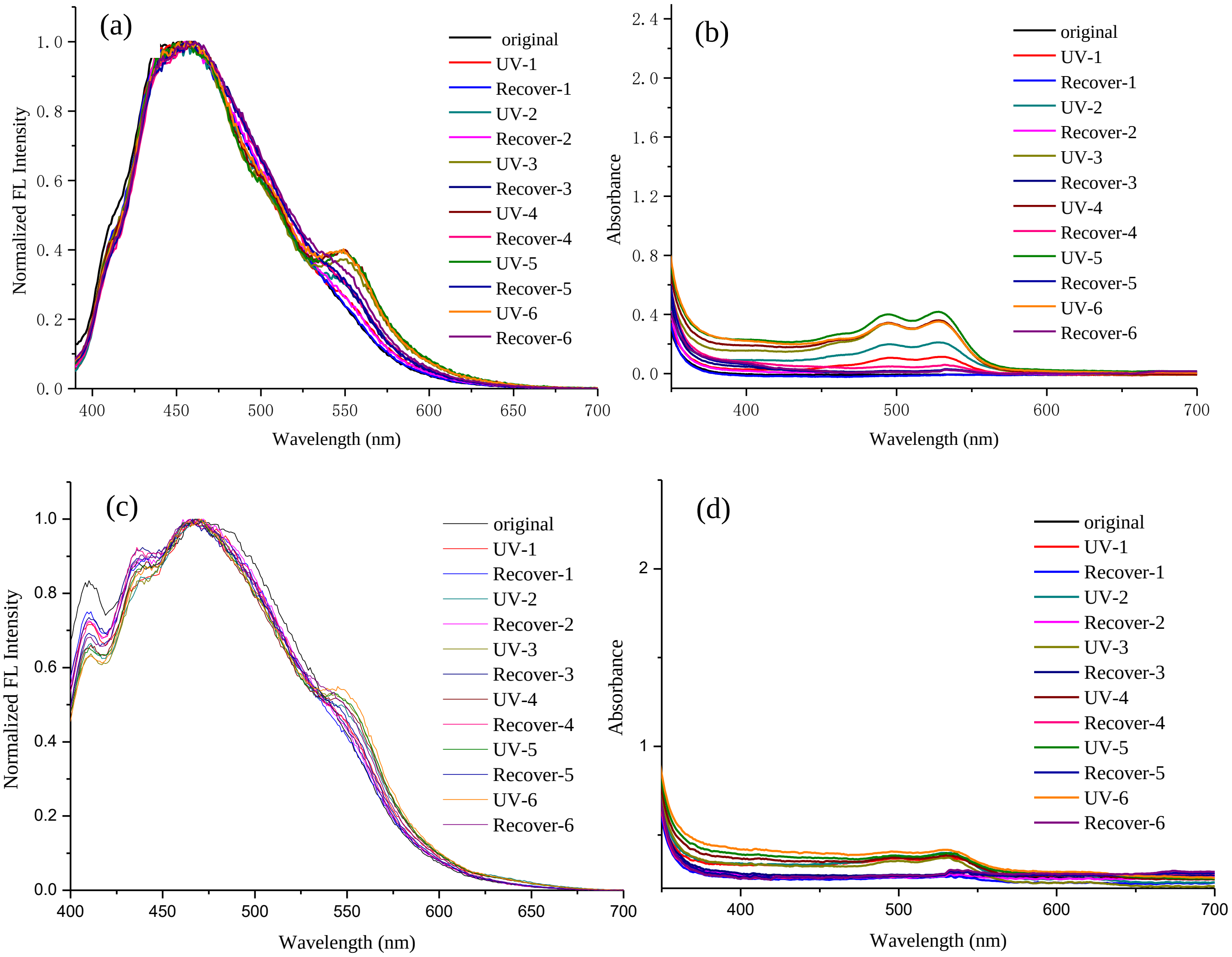


Figure S10. Fluorescence spectra of trans-RhRh (a) and cis-RhRh (c) in the cycle of UV light and room light; absorption spectra of trans-RhRh (b) and cis-RhRh (d) in the cycle of UV light and room light.

7. ^{1}HNMR of cis/trans-RhRh solution after UV irradiation

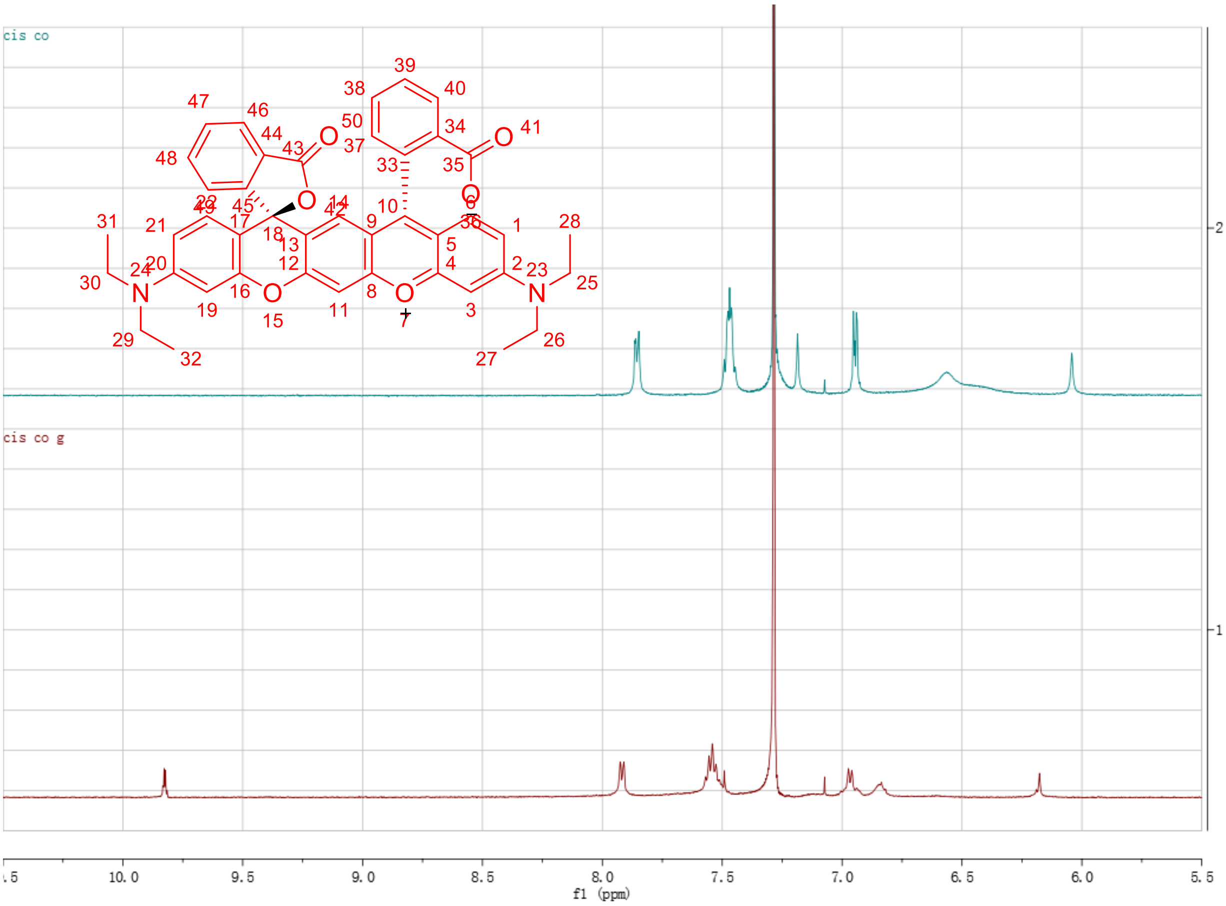


Figure S11. ^{1}HNMR of cis-RhRh solution in $CDCl_3$ before (up) and after (bottom) UV irradiation. (The integral of 9.83 peak is 0.22.)

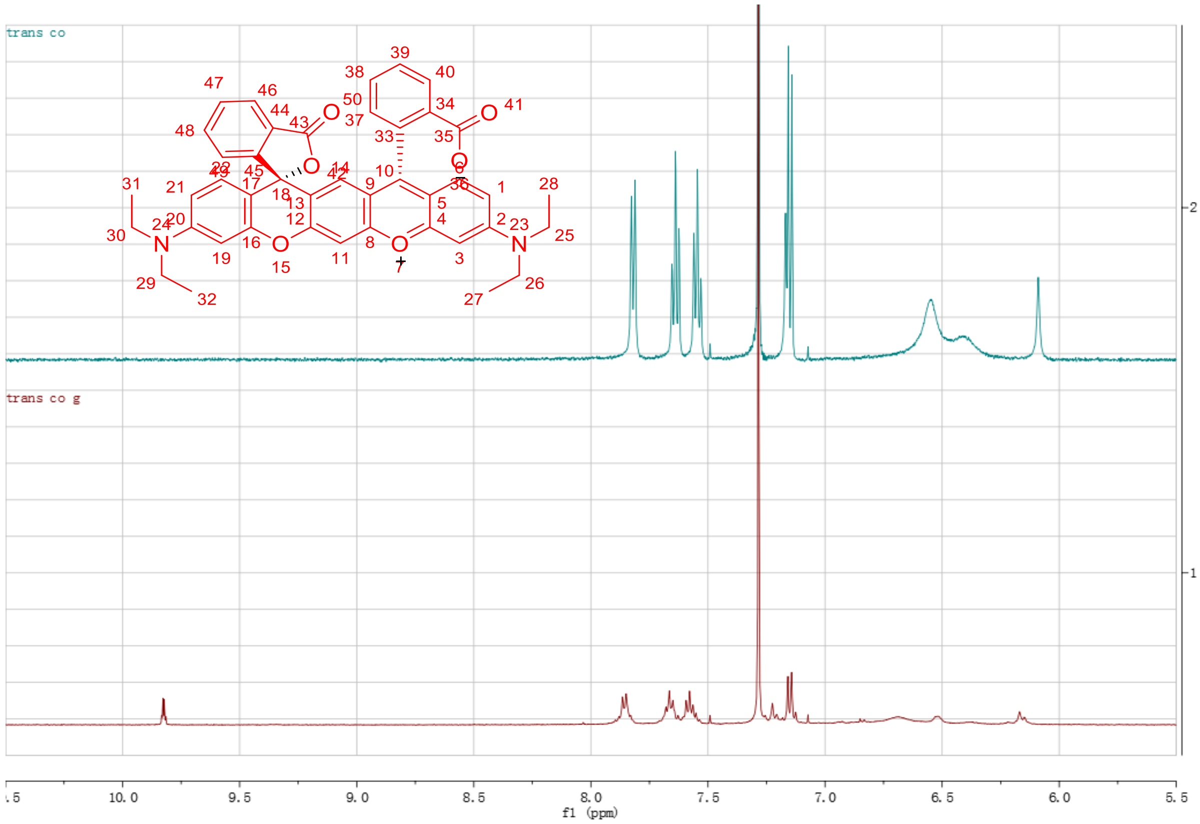


Figure S12. ^{1}HNMR of trans-RhRh solution in $CDCl_3$ before (up) and after (bottom) UV irradiation. (The integral of 9.83 peak is 0.25.)

7. cis/trans-RhRh in the single crystal

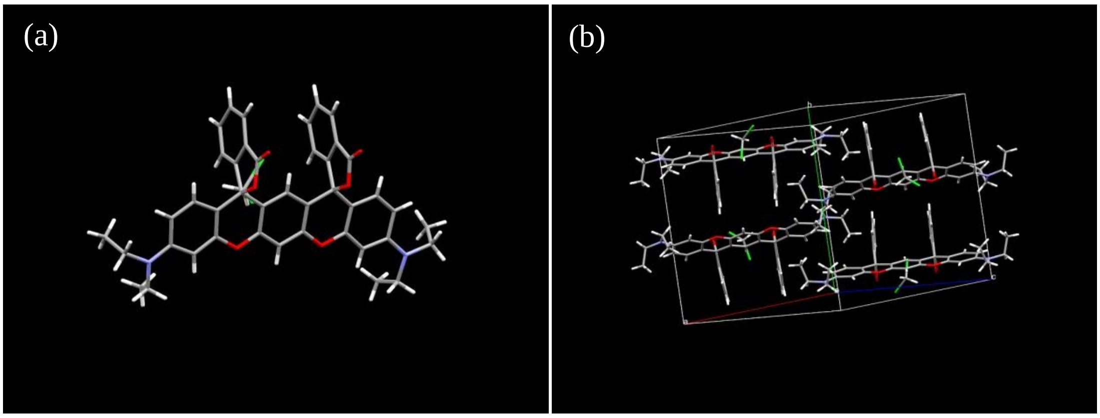


Figure S13. (a) The molecular geometry and (b) the unit cell in the cis-RhRh single crystal.

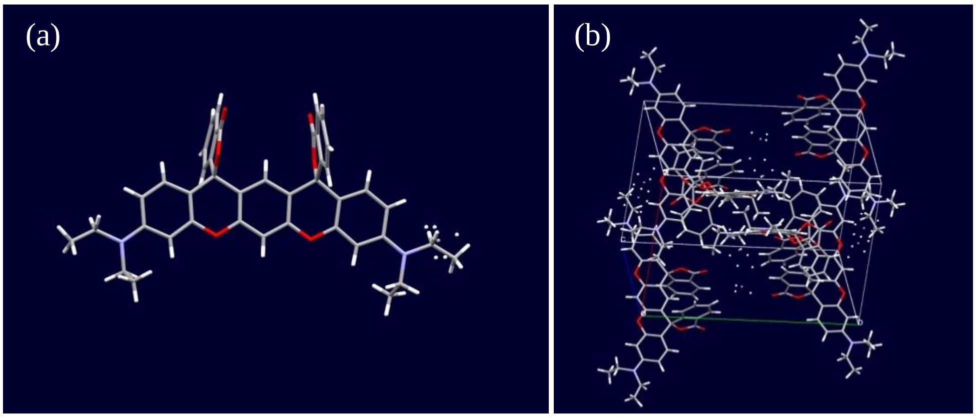


Figure S14. (a) The molecular geometry and (b) the unit cell in the trans-RhRh single crystal.

8. Photo-induced color change under room light

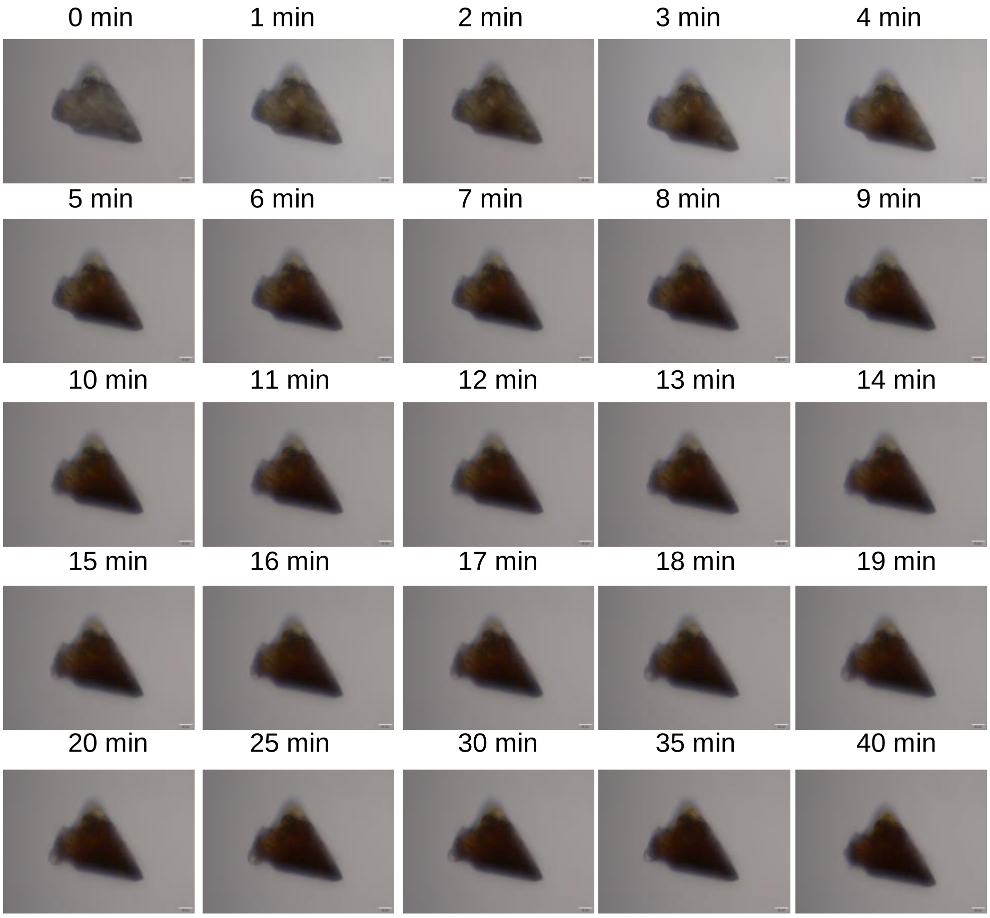


Figure S15. The cis-RhRh single crystal turned from colorless to dark red increasing the irradiation time.

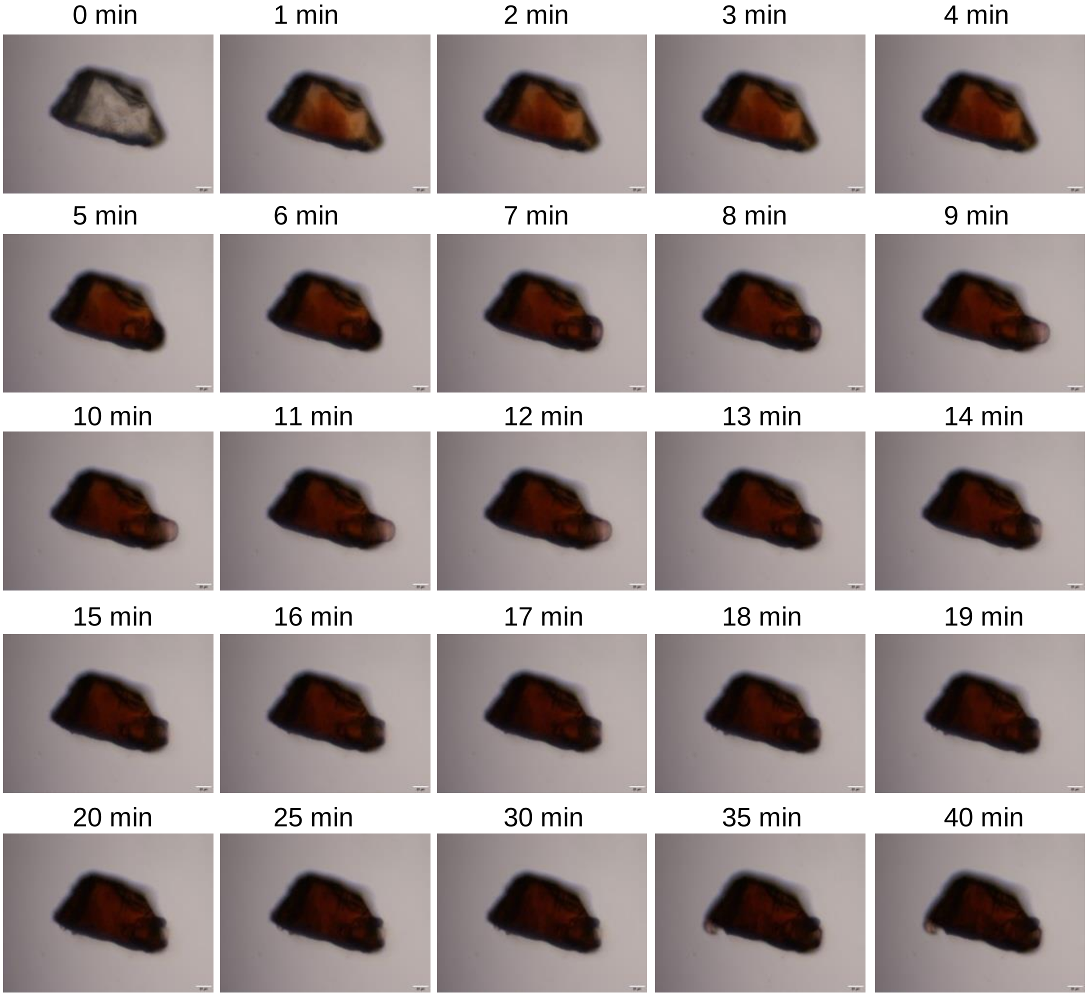


Figure S16. The trans-RhRh single crystal turned from colorless to dark red increasing the irradiation time.

9. Fluorescence spectra of cis- and trans-RhRh single crystal after UV

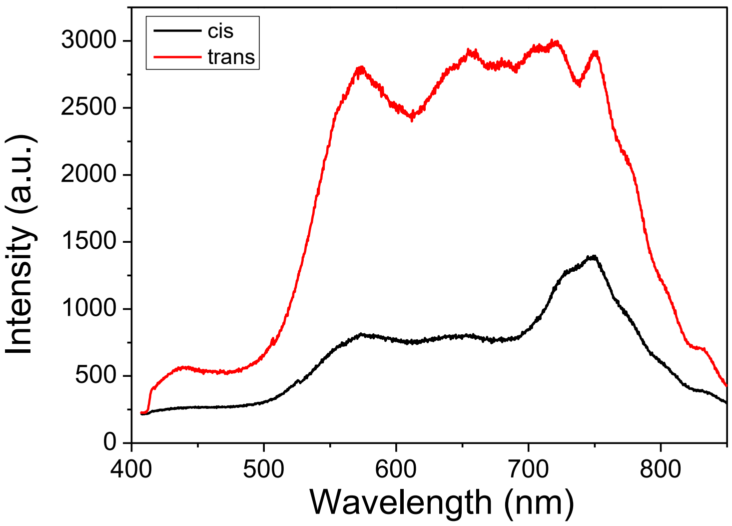


Figure S17. Fluorescence spectra of cis- and trans-RhRh single crystal after UV.

10. IR spectra

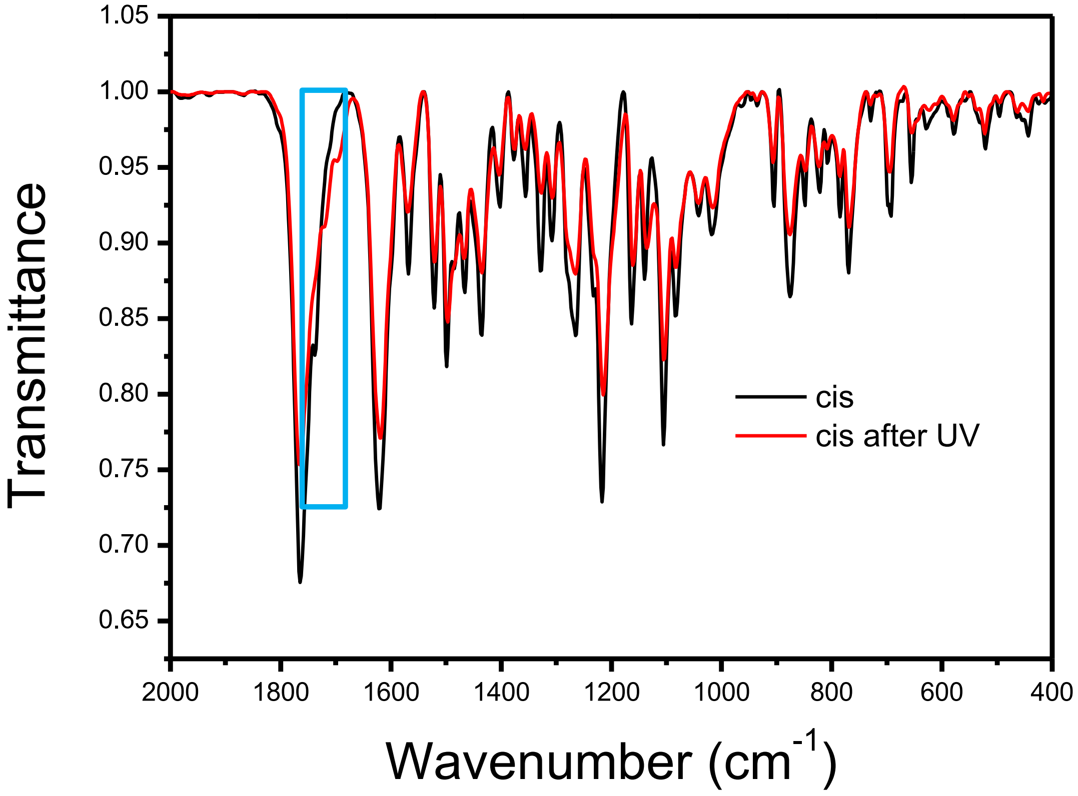


Figure S18. IR spectra of cis-RhRh single crystal before and after UV.

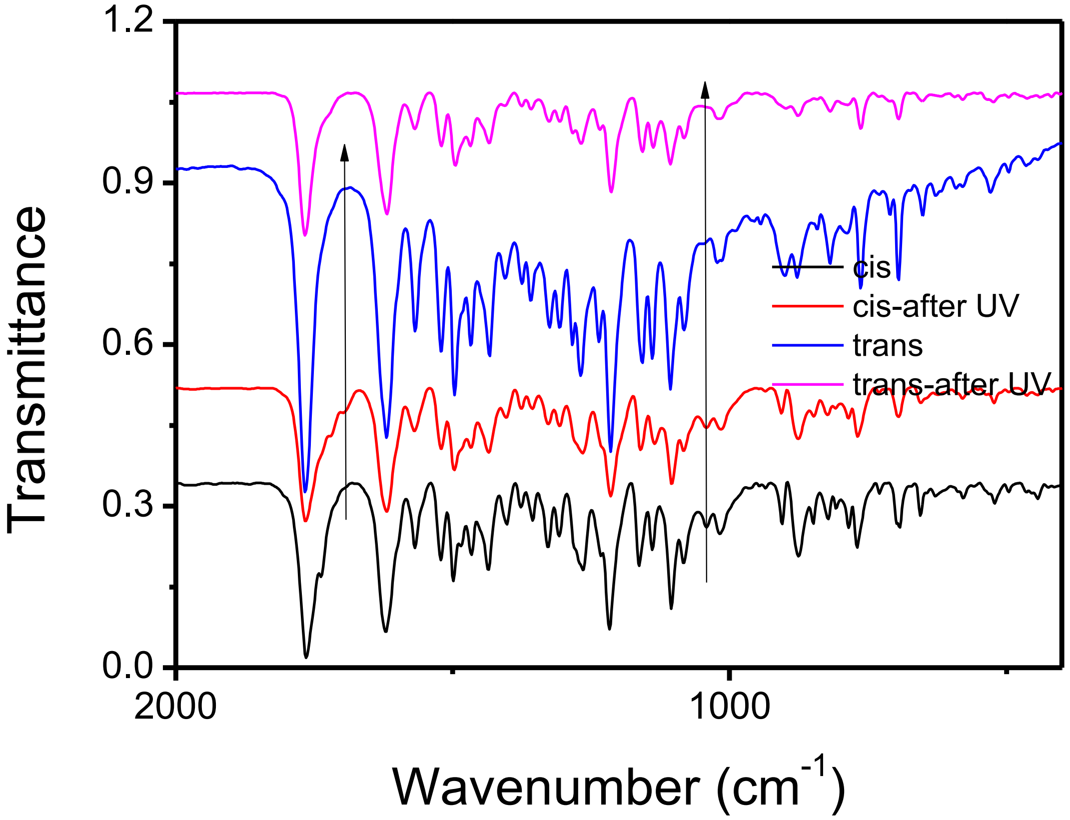


Figure S19. IR spectra of cis- and trans-RhRh single crystal before and after UV.

11. Prepared filter paper under room light

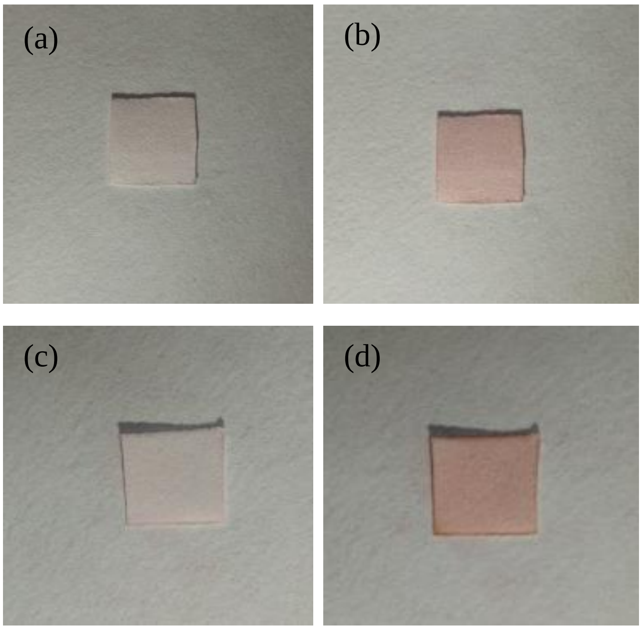
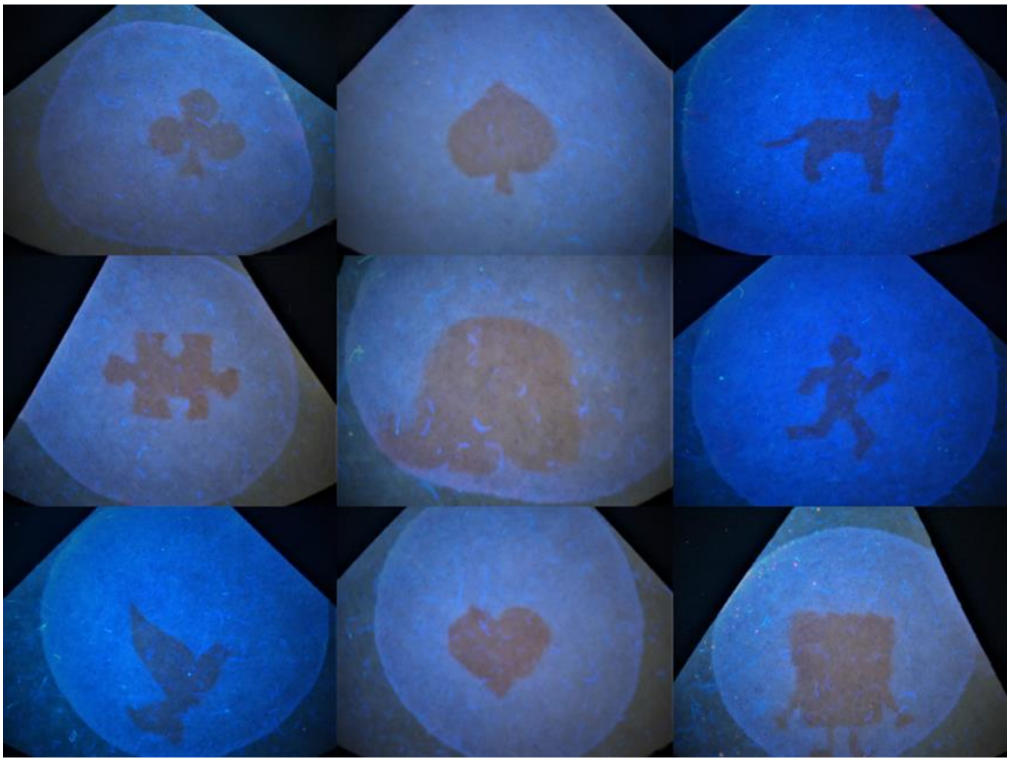


Figure S20. Prepared filter paper by droping cis/trans-RhRh DCM solution before (a) (c) and after (b) (d) UV. cis-RhRh: (a)(b), trans-RhRh: (c)(d)

12. Photoprinting on the filter paper



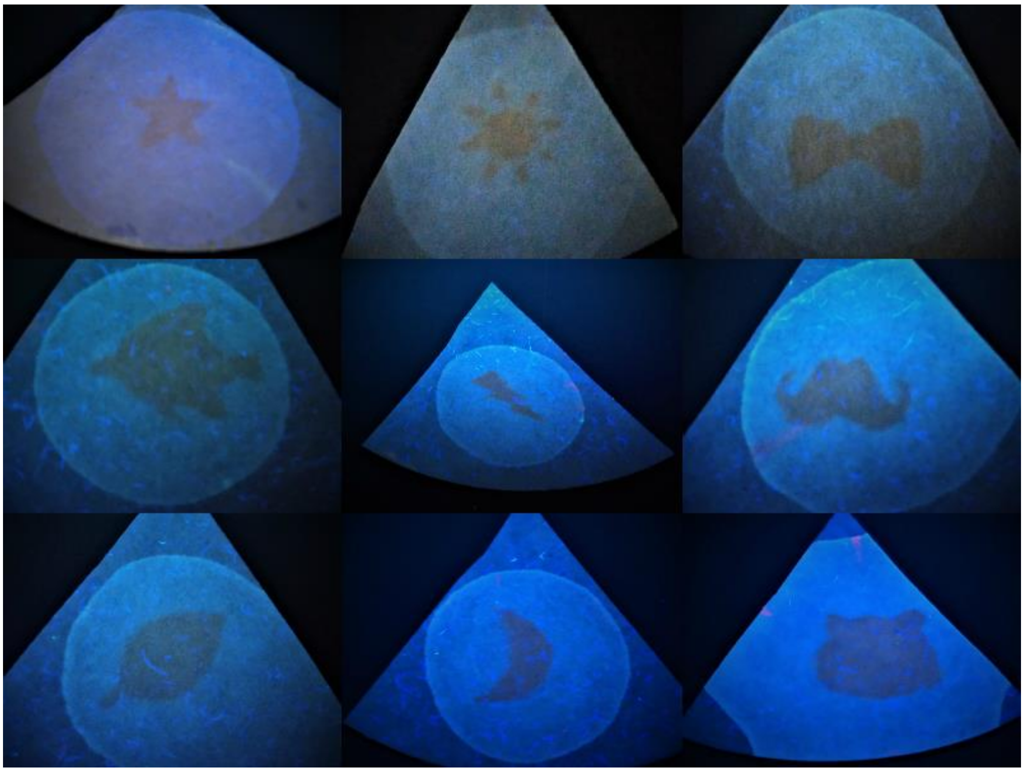


Figure S21. Different patterns were printed on the filter papers. cis-(up), trans-(down)

References

[1] C. Wang and K. M.-C. Wong, *Inorg. Chem.*, 2013, **52**, 13432-13441.