Supplementary Information

# Room Temperature Photochromism and Photoinduced Slow Magnetic Relaxation of Cyanometallic Supramolecular Hybrid Salts

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# 1. Experiment Section

### 1.1 Materials and instruments

2,2':6',2"-terpyridine (TPY), concentrated hydrochloric acid, potassium hexacyanoferrate, potassium hexacyanocobaltate were commercially available and used as received without further purification. The C, H, and N microanalyses were carried out with an Elementar Vario-EL CHNS elemental analyzer. The Fournier transform infrared (FT-IR) spectra were recorded from KBr pellets in the range 2300-400 cm<sup>-1</sup> on a PerkinElmer FT-IR spectrometer. Powder Xray diffraction (PXRD) patterns were obtained at room temperature on a Rigaku diffractometer using Cu  $K_{\alpha}$  radiation ( $\lambda$  = 1.540598 Å) at 40 kV and 26 mA scanning from 5-50 2 $\theta$  degree. Simulated PXRD patterns were gained using the Mercury Version 2020.3.0 software based on the single-crystal data. Thermogravimetric spectrum (TG) analysis was carried out on a TG209 F1 Libra device with N<sub>2</sub> atmosphere, and the sample was heated in an Al<sub>2</sub>O<sub>3</sub> crucible at the heating speed of 10 K<sup>-</sup>min<sup>-1</sup>. UV-vis spectra were recorded by the diffuse reflection mode with BaSO<sub>4</sub> as the reference on a Shimadzu UV-3600 Plus UV/VIS/NIR spectrometer, which is equipped with an integrating sphere. Electron paramagnetic resonance (EPR) data was achieved in the X band (frequency of microwave, 9.83 GHz) at room temperature on a Bruker Model A300 spectrometer with a 100 kHz magnetic field. The HF-EPR spectra were recorded using a locally developed spectrometer at the Wuhan National High Magnetic Field Center, China.<sup>1</sup> The microwaves of the transmission-type instrument are propagated by over-sized cylindrical light pipes. A UV LED lamp (365 nm, 10 W) was used to perform the irradiation at room temperature, whose distance from samples was set as 10 cm (~750 mW/cm<sup>2</sup>).

### 1.2 Synthesis Route

**Caution!** Cyanides are potentially poisonous compounds. Suitable precautions should be taken when handling them. It is of the utmost importance that all preparations be performed and all compounds stored in well-ventilated areas.

**Synthesis of TPY-2HCI-H**<sub>2</sub>**O.** Synthesize the precursor TPY-2HCI-H<sub>2</sub>O has been modified as detailed below.<sup>2</sup> Excess amount of concentrated hydrochloric acid was dropped into the acetonitrile (30 ml) solution of 2,2':6',2"-terpyridine (1mmol, 232 mg), resulting in orange suspension. After stirring for 30 min, the mixture was filtered and the solid product was dried in the air (yield ~62% based on 2,2':6',2"-terpyridine).

**Synthesis of (HTPY)(H<sub>2</sub>TPY)[Fe(CN)<sub>6</sub>]·5H<sub>2</sub>O (1).** Dry powder of TPY·2HCI·H<sub>2</sub>O (200 mg, ~0.6 mmol) and potassium hexacyanoferrate(III) (99 mg, 0.3 mmol) were dissolved in 20 ml and 5 ml of distilled deionized water respectively. During stirring, the clear solution of potassium hexacyanoferrate(III) was added dropwise to the solution of TPY·2HCI·H<sub>2</sub>O and yellow precipitate of **1** formed immediately. The solid product was filtered, washed with ethanol and dried in the air (yield ~73% based on K<sub>3</sub>[Fe(CN)<sub>6</sub>]). And the yellow stripe crystal can be obtained by slow diffusion of TPY·2HCI·H<sub>2</sub>O and potassium hexacyanoferrate(III) in distilled deionized water. The purple-red sample of **1UV** was obtained by irradiating the fine ground powder of **1** with a 365 nm LED lamp for about 5 hours in the ambient condition. Element analysis calcd(%) for C<sub>36</sub>H<sub>35</sub>FeN<sub>12</sub>O<sub>5</sub> (**1**): C 56.04; H 4.57; N 21.78; found (%): C. 56.13; H. 4.53; N. 21.98. Calcd(%) for C<sub>36</sub>H<sub>34.6</sub>FeN<sub>12</sub>O<sub>4.8</sub> (**1UV**): C 56.30; H 4.54; N 21.89; found (%): C. 56.75; H. 4.51; N. 21.21.

**Synthesis of (HTPY)(H<sub>2</sub>TPY)[Co(CN)<sub>6</sub>]·5H<sub>2</sub>O (2).** Dry powder of TPY·2HCl·H<sub>2</sub>O (200 mg, ~0.6 mmol) and potassium hexacyanocobaltate(III) (100 mg, 0.3 mmol) were dissolved in 20

ml and 5 ml of distilled deionized water respectively. During stirring, the clear solution of potassium hexacyanocobaltate (III) was added dropwise to the solution of TPY·2HCI·H<sub>2</sub>O and white precipitate of **2** formed immediately. The solid product was filtered, washed with ethanol and dried in the air (yield ~52% based on K<sub>3</sub>[Co(CN)<sub>6</sub>]). And the colourless stripe crystal can be obtained by slow diffusion of TPY·2HCI·H<sub>2</sub>O and potassium hexacyanocobaltate(III) in distilled deionized water. The orange sample of **2UV** was obtained by irradiating the fine ground powder of **2** with a 365 nm LED lamp for about 24 hours in the ambient condition. Element analysis calcd(%) for C<sub>36</sub>H<sub>35</sub>CoN<sub>12</sub>O<sub>5</sub> (**2**): C 55.82; H 4.55; N 21.70; found (%): C. 56.16; H. 4.18; N. 21.87. Calcd(%) for C<sub>36</sub>H<sub>33</sub>CoN<sub>12</sub>O<sub>4</sub> (**2UV**): C 57.14; H 4.40; N 22.21; found (%): C. 57.35; H. 4.23; N. 21.96.

### 1.3X-ray Crystallographic Study

Diffraction intensities were collected on a Bruker D8 QUEST diffractometer equipped with Mo- $K_{\alpha}$  ( $\lambda = 0.71073$  Å) high-brilliance  $l\mu$ S (microfocus source) radiation for **1** and **2** at 120 K. The structures were solved using intrinsic phasing methods (SHELXT 2014)<sup>3</sup> in the OLEX2 program<sup>4</sup>. All non-hydrogen atoms were refined anisotropically by least-squares on  $F^2$  using the SHELXTL program suite. Anisotropic thermal parameters were assigned to all nonhydrogen atoms. Hydrogen atoms on organic ligands were located from difference maps and refined with isotropic temperature factors and generated by the riding mode.<sup>5</sup> Data has been deposited at the Cambridge Structural Database with the following CCDC numbers: 2121540-2121541.

### **1.4 Computational Methods.**

All calculations were carried out using the Gaussian 09 program.<sup>6</sup> The widely used exchange correlation functional B3LYP<sup>7</sup> was chosen in view of its good compromise between accuracy and computational cost. The initial geometries were taken from the crystal structures in the Cambridge Crystallographic Data Centre (CCDC). The ground-state geometries were optimized in vacuum at the B3LYP/6-31+g(d) level and then electronic transitions were calculated by the TD-DFT approach<sup>8</sup> using the same functional and basic set as the ground-state geometries optimization. The singlet excited state geometries were optimized in vacuum by TD-DFT calculations at the B3LYP/6-31+g(d) level on the basis of the ground-state geometry.

#### **1.5 Magnetic Measurements**

Magnetic susceptibility measurements were collected using a Quantum Design MPMS3 SQUID VSM magnetometer at temperatures between 1.8 and 300 K and dc magnetic fields ranging from 0 to 7 T. AC magnetic susceptibility data measurements were performed on Quantum Design MPMS3 SQUID VSM magnetometer with a 1.5 Oe oscillating field at temperatures between 2 and 10 K. All data were corrected for the diamagnetic contribution calculated from the empirical measurements.

# 2. Quantum Chemical Calculations



**Figure S1** The optimized geometries of the selected pyridyl analogues at their first singlet excited state. BPY = 4,4'-bipyridine; HBPY<sup>+</sup> = 4,4'-bipyridin-1-ium; H<sub>2</sub>BPY<sup>2+</sup> = 4,4'-bipyridin-1,1'-diium; Phen = 1,10-phenanthroline; HPhen<sup>+</sup> = 1,10-phenanthrolin-1-ium; H<sub>2</sub>Phen<sup>2+</sup> = 1,10-phenanthrolin-1,1'-diium; TPY = 2,2':6',2"-terpyridine; HTPY<sup>+</sup> = [2,2':6',2"-terpyridin]-1-ium; H<sub>2</sub>TPY<sup>2+</sup> = [2,2':6',2"-terpyridine]-1,1"-diium.



**Figure S2** The HOMO-LUMO energy gaps calculated under the B3LYP/6-31+G(d) level for the first singlet excited states of the selected pyridyl analogues.

	BPY	HBPY⁺	H <sub>2</sub> BPY <sup>2+</sup>	Phen	HPhen⁺
HOMO / eV	-6.75	-9.70	-15.15	-6.35	-10.42
LUMO / eV	-2.40	-7.08	-11.58	-2.00	-6.95
gap / eV	4.34	2.62	3.57	4.36	3.47
	H <sub>2</sub> Phen <sup>2+</sup>	TPY	HTPY⁺	H <sub>2</sub> TPY <sup>2+</sup>	
HOMO / eV	-14.77	-6.32	-9.47	-13.74	
LUMO / eV	-11.22	-2.05	-6.76	-9.77	
gap / eV	3.54	4.27	2.72	3.97	

**Table S1** The calculated results of the frontier molecular orbitals for the first singlet excited states of the selected pyridyl analogues.

**Table S2a** The calculated excitation wavelengths and oscillator strengths for the ground states of selected pyridyl analogues.

Excited	BP	ſ	HBP	γ	H <sub>2</sub> BF	рү
State	$\lambda$ / nm	f	$\lambda$ / nm	f	λ / nm	f
ES1	292.82	0.0000	456.88	0.0006	263.00	0.0754
ES2	292.49	0.0042	385.07	0.0094	262.83	0.0143
ES3	267.74	0.0000	310.33	0.1405	242.61	0.3716
ES4	256.71	0.0678	301.82	0.1905	208.46	0.0082
ES5	255.94	0.4134	285.34	0.0217	208.10	0.0411
ES6	243.16	0.0000	255.77	0.0008	206.43	0.0000
ES7	243.13	0.0000	251.43	0.0014	198.91	0.0008
ES8	219.09	0.0000	249.75	0.0026	198.85	0.0000
ES9	207.73	0.3396	228.00	0.0914	197.50	0.0000
ES10	206.52	0.0000	219.12	0.0311	187.40	0.0030

Excited	Phe	en	Pł	nen	H <sub>2</sub> Ph	H <sub>2</sub> Phen	
State	λ / nm	λ / nm	$\lambda$ / nm	f	λ / nm	f	
ES1	310.30	310.30	363.61	0.0167	363.00	0.0153	
ES2	307.33	307.33	321.38	0.0390	317.96	0.0059	
ES3	305.99	305.99	316.46	0.0006	271.31	0.6289	
ES4	290.51	290.51	270.92	0.0011	264.45	0.0379	
ES5	277.50	277.50	270.05	0.4044	230.88	0.0087	
ES6	276.59	276.59	262.39	0.1312	225.02	0.0081	
ES7	262.29	262.29	238.71	0.0713	213.32	0.1396	
ES8	249.48	249.48	224.52	0.1575	212.47	0.2856	
ES9	235.96	235.96	219.98	0.0004	204.92	0.0002	
ES10	227.63	227.63	216.05	0.0618	202.40	0.0000	

**Table S2b** The calculated excitation wavelengths and oscillator strengths for the ground states of selected pyridyl analogues.

**Table S2c** The calculated excitation wavelengths and oscillator strengths for the ground states of selected pyridyl analogues.

Excited	TP۱	(	HTP	Ϋ́Υ	H <sub>2</sub> TF	рү
State	$\lambda$ / nm	f	$\lambda$ / nm	f	λ / nm	f
ES1	298.16	0.2494	436.16	0.0782	317.60	0.3781
ES2	292.87	0.0000	411.45	0.0000	286.25	0.1667
ES3	291.01	0.0027	342.31	0.0061	268.16	0.0025
ES4	286.21	0.1318	332.99	0.0674	255.33	0.0298
ES5	273.07	0.0006	323.62	0.0002	253.21	0.0103
ES6	266.88	0.0000	308.78	0.0006	253.15	0.0998
ES7	263.06	0.3502	302.03	0.0005	251.85	0.0040
ES8	252.81	0.0000	299.20	0.2635	244.65	0.2448
ES9	252.71	0.1904	282.03	0.2383	234.79	0.1161
ES10	249.66	0.0029	272.67	0.0597	228.43	0.0189

Excited	BP	ſ	HBP	γY	H <sub>2</sub> BF	H <sub>2</sub> BPY	
State	$\lambda$ / nm	f	$\lambda$ / nm	f	λ / nm	f	
ES1	371.81	0.0011	648.30	0.0002	421.07	0.0225	
ES2	301.13	0.0022	387.88	0.0078	302.91	0.4683	
ES3	284.43	0.0000	361.20	0.0000	297.90	0.0504	
ES4	277.52	0.4766	312.34	0.3350	233.50	0.0396	
ES5	275.09	0.0064	304.80	0.0113	232.71	0.0194	
ES6	261.16	0.0515	290.90	0.0017	219.99	0.0031	
ES7	237.76	0.0000	274.17	0.0060	217.89	0.0063	
ES8	227.50	0.0018	251.88	0.0035	212.08	0.1502	
ES9	224.16	0.0000	243.41	0.0061	206.96	0.0010	
ES10	218.41	0.0014	229.96	0.0903	197.91	0.0853	

**Table S3a** The calculated excitation wavelengths and oscillator strengths for the first excited states of selected pyridyl analogues.

**Table S3b** The calculated excitation wavelengths and oscillator strengths for the first excited states of selected pyridyl analogues.

Excited	Phe	en	Ph	Phen		hen
State	λ / nm	λ / nm	f	λ / nm	f	$\lambda$ / nm
ES1	371.94	371.94	436.55	0.0184	416.12	0.0172
ES2	343.83	343.83	347.07	0.0004	336.47	0.0011
ES3	318.76	318.76	336.36	0.0239	282.62	0.5876
ES4	315.94	315.94	282.29	0.4918	265.74	0.0225
ES5	309.00	309.00	278.49	0.0013	237.53	0.0059
ES6	294.37	294.37	262.86	0.0174	231.40	0.0335
ES7	270.79	270.79	249.64	0.1016	220.83	0.3559
ES8	258.97	258.97	231.64	0.0669	217.30	0.2816
ES9	247.21	247.21	224.25	0.0001	211.13	0.0003
ES10	237.63	237.63	221.79	0.1344	209.52	0.0000

Excited	TP	(	HTP	HTPY		H <sub>2</sub> TPY	
State	λ / nm	f	λ / nm	f	λ / nm	f	
ES1	386.09	0.0003	542.57	0.0543	353.30	0.4301	
ES2	336.99	0.0009	469.59	0.0000	305.48	0.1762	
ES3	313.19	0.2869	371.07	0.0068	275.26	0.0014	
ES4	292.60	0.0009	358.53	0.0720	270.83	0.0450	
ES5	292.27	0.1060	339.97	0.0004	265.40	0.0210	
ES6	275.16	0.0006	331.16	0.0003	264.44	0.2094	
ES7	272.15	0.5215	318.56	0.2829	255.77	0.0000	
ES8	269.63	0.0002	309.59	0.0005	253.56	0.1551	
ES9	263.22	0.0000	296.74	0.1643	243.51	0.1133	
ES10	261.77	0.0799	286.64	0.1608	233.97	0.0308	

**Table S3c** The calculated excitation wavelengths and oscillator strengths for the first excited states of selected pyridyl analogues.





**Figure S3** Stacking structure along the viewing direction for compound **2**. Hydrogen atoms and lattice water molecules are omitted and hexacyanocobaltate ions are represented as polyhedrons.



**Figure S4** Structure representation of **2** with conventional hydrogen bonding interactions (orange dash lines). Some atoms have been omitted for clear.

	1	2
Empirical formula	$C_{36}H_{35}FeN_{12}O_5$	$C_{36}H_{35}CoN_{12}O_5$
Formula weight	771.59	774.69
Temperature / K	120	120
Crystal system	Orthorhombic	orthorhombic
Space group	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>
a / Å	12.8975(5)	12.9135(5)
b/Å	13.0681(7)	13.0515(5)
c / Å	21.8101(11)	21.7223(9)
α/°	90	90
βl°	90	90
γ/°	90	90
Volume / Å <sup>3</sup>	3676.0(3)	3661.1(3)
Z	4	4
$ ho_{ m calc}g$ / $ m cm^3$	1.387	1.405
μ / mm <sup>-1</sup>	0.469	0.529
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.098	1.052
Final <i>R</i> indexes [I>=2σ (I)] <sup>a</sup>	R <sub>1</sub> = 0.0386, wR <sub>2</sub> = 0.0735	<i>R</i> <sub>1</sub> = 0.0214, <i>wR</i> <sub>2</sub> = 0.0511
Final <i>R</i> indexes [all data]	R <sub>1</sub> = 0.0470, wR <sub>2</sub> = 0.0756	<i>R</i> <sub>1</sub> = 0.0236, <i>wR</i> <sub>2</sub> = 0.0519
Flack parameter	0.008(6)	-0.005(3)

 Table S3
 Crystal data and structure refinement for 1 and 2.

<sup>a</sup>  $R_1 = \sum ||F_0| - |F_c|| / \sum |F_0|$ .  $wR_2 = [\sum w(F_0^2 - F_c^2)^2 / \sum w(F_0^2)^2]^{1/2}$ .

#### Table S4 Bond lengths for compound 1 and 2.

Bond length / Å	1 (M = Fe)	2 (M = Co)
M-C1	1.935(4)	1.889(2)
M-C2	1.950(4)	1.904(2)
M-C3	1.948(4)	1.898(2)
M-C4	1.941(4)	1.900(2)
M-C5	1.944(4)	1.899(2)
M-C6	1.930(3)	1.891(2)
Average	1.941	1.897

# 4. Chemical and Physical Characterization



**Figure S5** Thermogravimetric spectrum (TG) analysis for **1** (a) and **2** (b) before and after irradiation under N<sub>2</sub> atmosphere (10 K min<sup>-1</sup>). The weight loss of **1** (11.6 %) and **2** (11.2 %) are close to the weight percent of  $5H_2O$  in **1**(11.6 %) and **2** (11.7 %). The weight loss of **1UV** (7.5 %) and **2UV** (4.8 %) are lower than the nonirradiated samples because of the partial loss of the lattice H<sub>2</sub>O molecules after the irradiation.



**Figure S6** PXRD patterns for **1** (top) and **2** (bottom) before and after irradiation. For the irradiated samples kept in the dark for 9 months, the protruding new peak at about 12 degrees may be caused by the chemical weathering of the samples.



**Figure S7** Time-dependent UV-vis spectra of compound **1** upon irradiation. The inset: photograph showing the photo-colouration.



Figure S8 Time-dependent UV-vis spectra of compound 2 upon irradiation.



Figure S9 The Fe 2p XPS spectrum for compound 1 before and after irradiation.



**Figure S10** The N 1s XPS spectrum for compound **1** before (top) and after (bottom) irradiation.



**Figure S11** The C 1s XPS spectrum for compound **1** before (top) and after (bottom) irradiation.



**Figure S12** The N 1s XPS spectrum for compound **2** before (top) and after (bottom) irradiation.



**Figure S13** The C 1s XPS spectrum for compound **2** before (top) and after (bottom) irradiation.

		1			1UV	
	B.E. / eV	Area	FWHM / eV	B.E. / eV	Area	FWHM / eV
	709.143	17597.490	1.997	708.493	16466.3	1.587
Eo 2n	722.518	8798.743	2.630	709.574	7240.643	3.432
ге 2р	736.147	4437.537	5.259	721.015	6249.029	1.544
				722.611	9185.094	2.245
	397.247	16249.510	1.342	397.105	13435.290	1.329
N 10	398.730	8643.666	1.515	398.416	3813.750	1.119
IN 15	401.105	8563.686	1.379	399.629	15052.430	1.338
				401.181	2176.801	1.051
	284.704	49708.070	1.807	284.714	62296.080	1.707
C 1a	286.276	14163.890	1.498	286.018	17213.340	1.412
0 15	288.350	784.933	1.609	287.153	4098.316	2.631
	292.462	3627.595	2.841	292.432	4443.265	2.943

**Table S5** Binding energies, intensity areas and FWHM of the XPS spectra for 1 and 1UV.

**Table S6**Binding energies, intensity areas and FWHM of the XPS spectra for 2 and 2UV.

		2			2UV	
	B.E. / eV	Area	FWHM / eV	B.E. / eV	Area	FWHM / eV
	780.910	28090.880	1.255	780.940	28480.460	2.290
	795.905	14045.440	1.763	786.018	3524.246	4.556
C0 2p				796.053	14240.230	2.427
				802.461	1551.749	3.957
	397.210	22917.920	1.096	397.177	9354.651	1.390
N 10	398.707	14699.510	1.615	398.411	9834.626	1.459
IN 15	401.056	12595.710	1.210	399.499	16684.100	1.490
				400.982	3490.481	1.742
	284.728	79362.930	1.623	284.686	73285.150	1.771
C 1a	285.989	8876.896	4.406	285.990	21602.480	1.422
C IS	286.236	21506.660	1.232	287.368	6035.013	2.250
	292.665	2873.392	1.889	292.217	3127.216	2.214



**Figure S14** Evolution of the IR spectrum between the range of 400-1800 cm<sup>-1</sup> for **1** in the KCI matrix upon irradiation.



**Figure S15** Evolution of the IR spectrum between the range of 400-1800 cm<sup>-1</sup> for **2** in the KCI matrix upon irradiation.



Figure S16 EPR spectra for 1 and 1UV at RT.



Figure S17 EPR spectra for 1UV kept in the dark after 2 months at RT.



Figure S18 EPR spectra for 2UV kept in the dark after 2 months at RT.



Figure S19 EPR spectra for 1 and 1UV at 2K.

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Figure S20 EPR spectrum for 2UV at 2K.

# 5. Magnetic Study



**Figure S21** Variable-temperature molar magnetic susceptibility data for **1**, **1UV** and **1UV** kept in the dark after 2 months and 9 months.



**Figure S22** Magnetic hysteresis loops continuously collected with a sweep rate of 200 Oe/s for **1** and **1UV** at 2 K.



**Figure S23** Variable-field magnetization data collected from 0 to 7 T in steady fields for **1** (left) and **1UV** (right).



**Figure S24** Temperature-dependence of the in-phase ( $\chi'_m$ ) and out-of-phase ( $\chi''_m$ ) susceptibilities with indicated ac frequencies under a zero dc field (left) and a 5 kOe dc field (right) for **1**.



**Figure S25** Temperature-dependence of the in-phase ( $\chi'_m$ ) and out-of-phase ( $\chi''_m$ ) susceptibilities with indicated ac frequencies under a zero dc field (left) and a 5 kOe dc field (right) for **1UV**.



**Figure S26** Frequency-dependence of the in-phase  $(\chi'_m)$  and out-of-phase  $(\chi''_m)$  susceptibilities under a 5 kOe dc field (right) for **1** (a) and **1UV** (b).



**Figure S27** Variable-temperature molar magnetic susceptibility data for **2**, **2UV** and **2UV** kept in the dark after 2 months and 9 months.



Figure S28 Variable-field magnetization data collected from 0 to 7 T in steady fields for 2UV.



**Figure S29** Temperature-dependence of the in-phase ( $\chi'_m$ ) and out-of-phase ( $\chi''_m$ ) susceptibilities with indicated ac frequencies under a zero dc field for **2UV**.



**Figure S30** Frequency-dependence of the in-phase ( $\chi'_m$ ) and out-of-phase ( $\chi''_m$ ) susceptibilities under a 5 kOe dc field for **2UV**.



**Figure S31** Magnetic hysteresis loops continuously collected with a sweep rate of 200 Oe/s for **2UV** at 2 K.

# 6. Reference

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