Electronic Supplementary Material (ESI) for Dalton Transactions.

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A novel photochromic hybrid containing trinuclear $[Cd_3Cl_{12}]^{6-}$ clusters and protonated tripyridyl-triazines

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Content

1. Experimental Section

Materials and Methods

All reagents and solvents were used as received. Elemental analyses (C, H, N) were performed on a Perkin-Elmer 240 elemental analyzer. FT-IR spectra were recorded in the range 4000-400 cm^{-1} on a Nicolet 5DX spectrometer using KBr pellets as the matrixes (Fig. S1). Powder X-ray diffraction (PXRD) patterns were collected on a Rigaku Ultima IV-185 diffractometer at ambient temperature. Thermogravimetric analysis-differential scanning calorimetry (TG-DSC) data were done on a HCT-2 thermogravimetric analyzer under N_2 atmosphere (100 cm^3 min^{-1}) at a heating rate of 10 ^oC min^{-1} (Figure S6). UV-vis absorption spectra were recorded in the wavelength range of 200-900 nm at room temperature on a METASH UV-9000S UV-vis spectrophotometer equipped with an integrating sphere. A $BaSO_4$ plate was used as a reference (100% reflectance), on which the finely ground powder of the samples were coated. Electron paramagnetic resonance (EPR) spectra were recorded on a Bruker A300-10/12 electron paramagnetic resonance spectrometer at ambient temperature. X-ray photoelectron spectroscopy (XPS) was performed with a Kratos AXIS ULTRA X-ray photoelectron spectrometer using Al Kα radiation (λ = 8.357 Å). All XPS spectra were referenced to the C1s neutral carbon peak at 284.7 eV in order to compensate for surface charging effects.

Preparation of $\{[H_3TPT]_2[Cd_3Cl_{12}]\}$ (1)

A mixture of TPT (0.05 mmol, 15mg), $CdCl_2 \bullet 2.5H_2O$ (0.15 mmol, 34 mg), benzyl alcohol (5 mL) and concentrated HCl (0.5 mL, 37%) was stirred for 30 min at room temperature. After about three days, colorless block-shaped crystals of **1** were obtained in yield of 45.5% (based on 4-TPT). Anal. Calcd for $C_{36}H_{30}N_{12}Cd_3Cl_{12}$: C 31.03, H 2.17, N 12.06%. Found: C 31.07, H 2.12, N 12.03%. IR data (KBr, cm^{-1}): 3431(m), 3053(m), 2929(w), 2371(w), 2067(w), 2004(w), 1943(w), 1621(m), 1553(s), 1397(s), 1304(m), 1243(m), 1167(w), 1091(w), 1044(w), 1007(w), 858(w),777(s), 666(m), 622(m), 492(w), 443(w).

Single Crystal X-ray Structure Determination and Refinement

Crystal data of **1** was collected at 273 K on a Bruker D8 Venture diffractometer equipped with focusing mirrors with MoK_α (λ = 0.71073 Å) radiation.[S1] An empirical absorption correction was applied to the data. SHELXTL-97 program was used to solve the structure.[S2,S3] Details of single crystal data for **1** are summarized in Table S1. The selected bond lengths and angles are given in Table S2. The hydrogen bonds are given in Table S3. Full crystallographic data has been deposited with the CCDC 1935646 for **1**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* https://www.ccdc.cam.ac.uk/deposit/upload.

References

S1. *CrysAlisPro*, version 1.171.33.56, Oxford Diffraction Ltd., Oxfordshire, UK, 2010.

S2. G. M. Sheldrick, *Acta Crystallogr. Sect. A: Found. Crystallogr*. 2008, **A64**, 112–122.

S3. G. M. Sheldrick, *SHELXS-97*, A Program for X-ray Crystal Structure Solution, and SHELXL-97, A Program for X-ray Structure Refinement; Göttingen University: Germany, 1997.

2. Figures

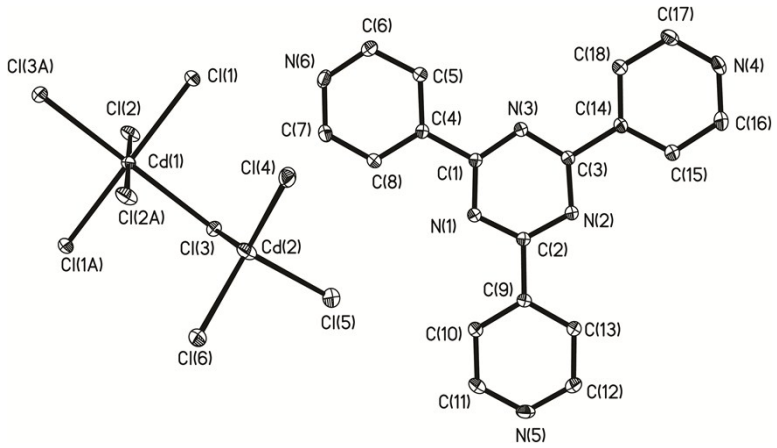

Fig. S1 The asymmetric unit of **1**.

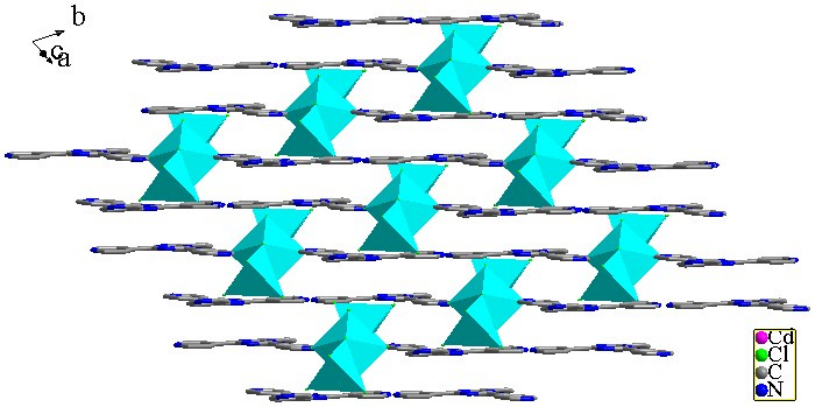

Fig. S2 Packing diagram of **1** showing the position of $[H_3TPT]^{3+}$ cations and $[Cd_3Cl_{12}]^{6-}$ anionic clusters.

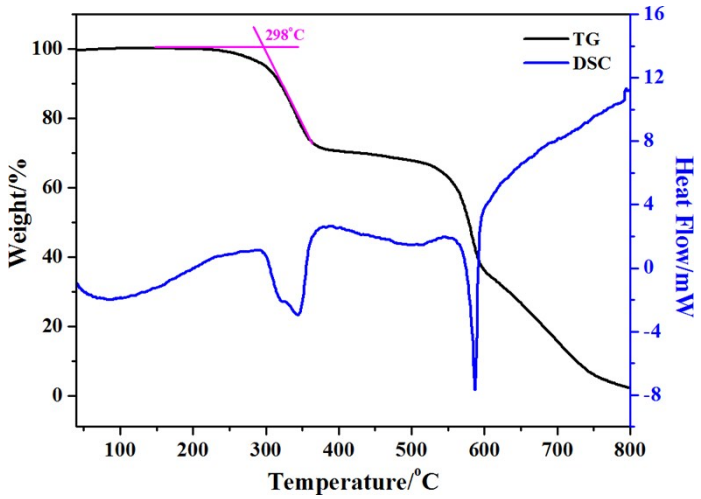

Fig. S3 Thermo-gravimetric (TG) and Differential scanning calorimetry (DSC) curve of **1**.

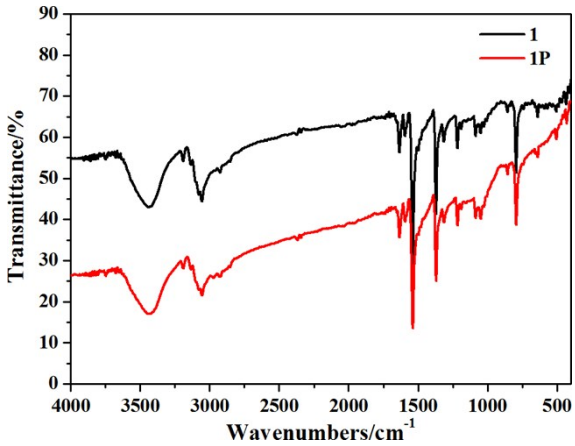

Fig. S4 IR spectra of **1** and **1P**.

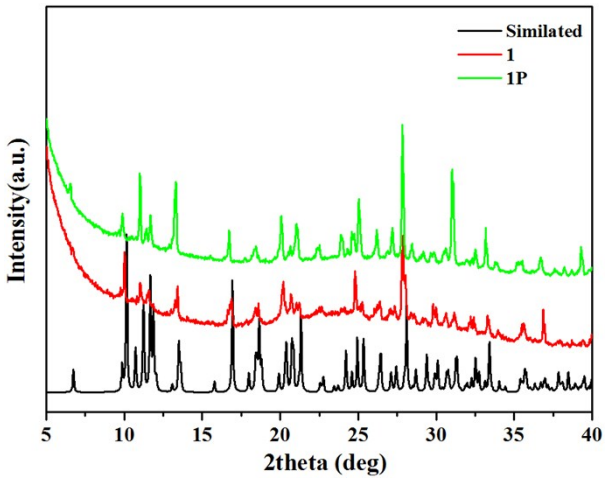

Fig. S5 Powder X-ray diffraction (PXRD) patterns of **1** and **1P** at room temperature.

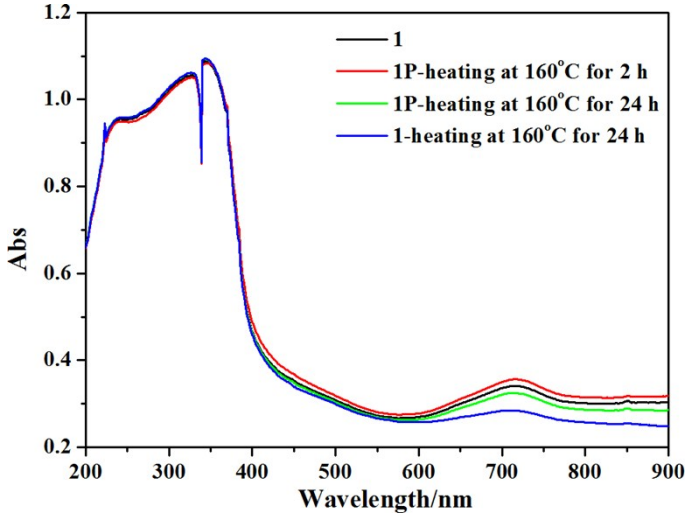

Fig. S6 UV–vis absorption spectra of **1**, **1**-heating at 160°C for 2 h, **1**-heating at 160°C for 24 h and **1P**-heating at 160°C for 24 h.

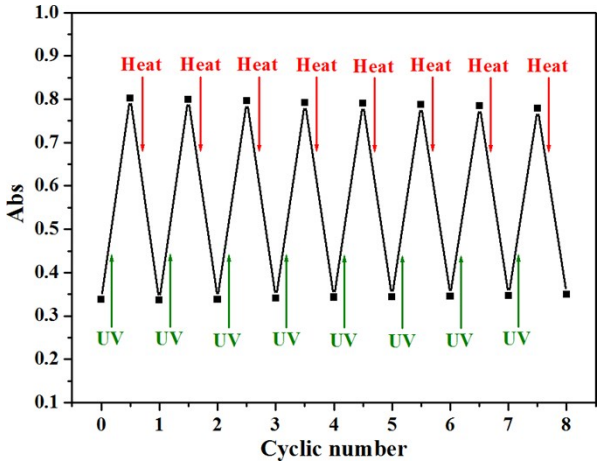

Fig. S7 The coloration-decoloration processes with repeated UV irradiation/heating of **1**.

3. Tables

Table S1. Crystallographic data and refinement parameters of **1** and **1P**.

Compounds	**1**	**1P**
CCDC code	1935646	1947057
Temperature (K)	273(2)	273(2)
Empirical formula	$C_{36}H_{30}Cd_3Cl_{12}N_{12}$	$C_{36}H_{30}Cd_3Cl_{12}N_{12}$
Formula weight	1393.32	1393.32
Crystal size (mm)	0.50 x 0.28 x 0.18	0.54 x 0.36 x 0.20
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	9.8035(15)	9.819(4)
b (Å)	9.9473(16)	9.940(4)
c (Å)	13.347(2)	13.353(6)
α (°)	84.524(3)	84.328(8)
β (°)	79.160(3)	79.004(7)
γ (°)	64.263(3)	64.141(7)
V (Å^3)	1151.4(3)	1151.0(8)
Z	1	1
D_c (g cm^{-3})	2.009	2.010
F(000)	678	678
μ (mm^{-1})	2.114	2.115
ϑ range (°)	2.77 to 28.33	3.01 to 28.33
Reflections collected	17891	16637
Unique reflections	5655	5510
R_{int}	0.0181	0.0191
Goodness-of-fit on F^2	1.087	1.120
R_1/wR_2, $[I \geq 2\sigma(I)]^{a,b}$	0.0228/0.0587	0.0264/0.0660
R_1/wR_2, (all data)	0.0250/0.0598	0.0275/0.0666
$\Delta\rho_{max}/\Delta\rho_{min}$ (e Å^{-3})	0.880/-1.278	0.946/-1.086

[a] $R_1 = \sum||F_o|-|F_c||/\sum|F_o|$ [b] $wR_2 = [\sum w(F_o^2-F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$

Table S2. Selected bond lengths (Å) and angles (°) of **1** and **1P**.

Compound **1**			
Cd(1)-Cl(1)#1	2.6128(5)	Cd(1)-Cl(1)	2.6128(6)
Cd(1)-Cl(2)#1	2.6406(6)	Cd(1)-Cl(2)	2.6406(6)
Cd(1)-Cl(3)	2.6721(5)	Cd(1)-Cl(3)#1	2.6721(5)
Cd(2)-Cl(4)	2.4367(6)	Cd(2)-Cl(6)	2.4479(6)
Cd(2)-Cl(5)	2.5249(7)	Cd(2)-Cl(3)	2.5688(6)
Cl(1)#1-Cd(1)-Cl(1)	180.000(1)	Cl(1)#1-Cd(1)-Cl(2)#1	87.589(19)
Cl(1)-Cd(1)-Cl(2)#1	92.411(19)	Cl(1)#1-Cd(1)-Cl(2)	92.411(19)
Cl(1)-Cd(1)-Cl(2)	87.589(18)	Cl(2)#1-Cd(1)-Cl(2)	180.000(1)
Cl(1)#1-Cd(1)-Cl(3)	88.222(16)	Cl(1)-Cd(1)-Cl(3)	91.778(16)
Cl(2)#1-Cd(1)-Cl(3)	86.25(2)	Cl(2)-Cd(1)-Cl(3)	93.75(2)
Cl(1)#1-Cd(1)-Cl(3)#1	91.778(16)	Cl(1)-Cd(1)-Cl(3)#1	88.222(16)
Cl(2)#1-Cd(1)-Cl(3)#1	93.75(2)	Cl(2)-Cd(1)-Cl(3)#1	86.25(2)
Cl(3)-Cd(1)-Cl(3)#1	180.000(1)	Cl(4)-Cd(2)-Cl(6)	117.28(2)
Cl(4)-Cd(2)-Cl(5)	104.02(2)	Cl(6)-Cd(2)-Cl(5)	99.71(2)
Cl(4)-Cd(2)-Cl(3)	123.59(2)	Cl(6)-Cd(2)-Cl(3)	113.51(2)
Cl(5)-Cd(2)-Cl(3)	89.79(2)	Cd(2)-Cl(3)-Cd(1)	101.493(19)
Symmetry code: #1 -x+2,-y+2,-z+1.			

Compound **1P**			
Cd(1)-Cl(1)#1	2.6124(10)	Cd(1)-Cl(1)	2.6124(10)
Cd(1)-Cl(2)#1	2.6385(9)	Cd(1)-Cl(2)	2.6385(9)
Cd(1)-Cl(3)	2.6724(10)	Cd(1)-Cl(3)#1	2.6724(10)
Cd(2)-Cl(4)	2.4360(11)	Cd(2)-Cl(6)	2.4506(9)
Cd(2)-Cl(5)	2.5266(11)	Cd(2)-Cl(3)	2.5638(9)
Cl(1)#1-Cd(1)-Cl(1)	180.0	Cl(1)#1-Cd(1)-Cl(2)	87.44(3)
Cl(1)-Cd(1)-Cl(2)	92.56(3)	Cl(1)#1-Cd(1)-Cl(2)#1	92.56(3)
Cl(1)-Cd(1)-Cl(2)#1	87.44(3)	Cl(2)-Cd(1)-Cl(2)#1	180.0
Cl(1)#1-Cd(1)-Cl(3)#1	88.21(3)	Cl(1)-Cd(1)-Cl(3)#1	91.79(3)
Cl(2)-Cd(1)-Cl(3)#1	86.19(4)	Cl(2)#1-Cd(1)-Cl(3)#1	93.81(4)

Cl(1)#1-Cd(1)-Cl(3)	91.79(3)	Cl(1)-Cd(1)-Cl(3)	88.21(3)
Cl(2)-Cd(1)-Cl(3)	93.81(4)	Cl(2)#1-Cd(1)-Cl(3)	86.19(4)
Cl(3)#1-Cd(1)-Cl(3)	180.0	Cl(4)-Cd(2)-Cl(6)	117.50(3)
Cl(4)-Cd(2)-Cl(5)	103.86(3)	Cl(6)-Cd(2)-Cl(5)	99.69(4)
Cl(4)-Cd(2)-Cl(3)	123.54(3)	Cl(6)-Cd(2)-Cl(3)	113.52(3)
Cl(5)-Cd(2)-Cl(3)	89.55(3)	Cd(2)-Cl(3)-Cd(1)	101.26(3)

Symmetry code: #1 -x+2,-y+2,-z+1.

Table S3 Hydrogen bonds of **1**.

Compound **1**				
D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)
C(6)-H(6)...Cl(2)#2	0.93	2.64	3.398(2)	138.8
C(6)-H(6)...Cl(4)#3	0.93	2.66	3.328(2)	129.3
C(7)-H(7)...Cl(3)	0.93	2.78	3.690(2)	166.8
C(8)-H(8)...Cl(5)	0.93	2.79	3.550(2)	139.7
C(10)-H(10)...Cl(5)	0.93	2.79	3.656(2)	155.1
C(11)-H(11)...Cl(5)#4	0.93	2.82	3.723(2)	163.4
C(12)-H(12)...Cl(1)#5	0.93	2.80	3.460(2)	129.2
C(12)-H(12)...Cl(4)#6	0.93	2.59	3.354(2)	140.3
C(15)-H(15)...Cl(5)#6	0.93	2.99	3.657(2)	129.9
C(16)-H(16)...Cl(6)#7	0.93	2.72	3.309(2)	121.9
C(16)-H(16)...Cl(6)#6	0.93	2.67	3.444(2)	141.0
N(4)-H(4)...Cl(2)#8	0.86	2.55	3.2468(18)	138.6
N(4)-H(4)...Cl(6)#7	0.86	2.64	3.2616(18)	129.7
N(5)-H(5A)...Cl(1)#5	0.86	2.95	3.5250(18)	126.2
N(5)-H(5A)...Cl(3)#4	0.86	2.46	3.2237(18)	148.5
N(6)-H(6A)...Cl(1)	0.86	2.47	3.2026(17)	142.9
N(6)-H(6A)...Cl(4)#3	0.86	2.85	3.4093(18)	124.7

Symmetry code: #1 -x+2,-y+2,-z+1; #2 x,y-1,z; #3 -x+2,-y+1,-z+1; #4 -x+1,-y+2,-z+2; #5 x-1,y,z+1; #6 -x+1,-y+1,-z+2; #7 x-1,y-1,z; #8 -x+1,-y+1,-z+1

Compound **1P**				
D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)
N(6)-H(6A)...Cl(4)#2	0.86	2.84	3.408(2)	124.6
N(6)-H(6A)...Cl(1)#1	0.86	2.48	3.203(2)	142.8
N(5)-H(5A)...Cl(3)#3	0.86	2.46	3.224(2)	148.4
N(5)-H(5A)...Cl(1)#3	0.86	2.95	3.526(2)	126.3
N(4)-H(4)...Cl(6)#4	0.86	2.64	3.256(2)	129.9
N(4)-H(4)...Cl(2)#5	0.86	2.56	3.258(2)	138.7
C(16)-H(16)...Cl(6)#6	0.93	2.66	3.437(3)	141.0
C(16)-H(16)...Cl(6)#4	0.93	2.73	3.310(3)	121.5
C(15)-H(15)...Cl(5)#6	0.93	2.99	3.655(3)	130.1
C(12)-H(12)...Cl(4)#6	0.93	2.59	3.354(3)	140.1
C(12)-H(12)...Cl(1)#3	0.93	2.80	3.461(3)	129.3
C(11)-H(11)...Cl(5)#3	0.93	2.82	3.722(3)	163.6
C(10)-H(10)...Cl(5)	0.93	2.79	3.659(3)	155.1
C(8)-H(8)...Cl(5)	0.93	2.79	3.549(3)	139.9
C(7)-H(7)...Cl(3)	0.93	2.78	3.695(3)	166.7
C(6)-H(6)...Cl(4)#2	0.93	2.66	3.326(2)	129.2
C(6)-H(6)...Cl(2)#7	0.93	2.64	3.399(3)	139.0

Symmetry code: #1 -x+2,-y+2,-z+1; #2 -x+2,-y+1,-z+1; #3 -x+1,-y+2,-z+2; #4 x-1,y-1,z; #5 -x+1,-y+1,-z+1; #6 -x+1,-y+1,-z+2; #7 x,y-1,z.