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Supporting Information for

# Three-component D-A hybrid heterostructures with enhanced photochromic, photomodulated luminescent and selectively anion-sensing properties

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1. The additional crystal figure for 1-D channel and electron transfer



Fig. S1. The 1-D channels for hybrid 1 view along *b*-axis.



Fig. S2. The electron transfer orientation diagrams of  $[Co(CN)_6]^{3-}$  and Bcebpy ligands in hybrid 1.

## 2. Crystal data and structure refinement

Table S1: Crystal data and structure refinement for hybrids 1-3.

Identification code	1	2	3
Empirical formula	C <sub>20</sub> H <sub>26</sub> CoEuN <sub>8</sub> O <sub>11</sub>	C <sub>20</sub> H <sub>22</sub> CoDyN <sub>8</sub> O <sub>9</sub>	C <sub>20</sub> H <sub>24.5</sub> CoN <sub>8</sub> O <sub>10.5</sub> Sm
Formula weight	763.36	739.88	754.25
Temperature/K	293(2)	293(2)	296.15
Crystal system	monoclinic	monoclinic	monoclinic
Space group	<i>C2/c</i>	C2/c	C2/c
a/Å	31.279(4)	31.279(5)	31.267(2)
b/Å	11.3928(6)	11.3714(10)	11.4024(6)
c/Å	21.323(3)	21.267(4)	21.1252(14)
α/°	90	90	90
β/°	130.59(2)	130.46(3)	130.659(2)
γ/°	90	90	90
Volume/Å <sup>3</sup>	5770.4(18)	5756(2)	5713.4(6)
Z	8	8	8
$\rho_{calc} g/cm^3$	1.757	1.708	1.754
$\mu/mm^{-1}$	2.796	3.211	2.682
F(000)	3024.0	2904.0	2988.0
Reflections collected	23184	22758	33182
Independent reflections	6562	5090	5042
Data/restraints/parameters	6562/0/387	5090/7/361	5042/2/395
Goodness-of-fit on F <sup>2</sup>	1.085	1.049	1.043
Final R indexes	$R_1 = 0.0367,$	$R_1 = 0.0667,$	$R_1 = 0.0283,$
$[I \ge 2\sigma(I)]$	$wR_2 = 0.0998$	$wR_2 = 0.1912$	$wR_2 = 0.0658$
Final R indexes [all data]	$R_1 = 0.0554,$	$R_1 = 0.0918,$	$R_1 = 0.0329,$
i mai it muckes [an uata]	$wR_2 = 0.1118$	$wR_2 = 0.2527$	$wR_2 = 0.0692$

# 3. Infrared spectral analysis



Figure S3. Infrared spectrum before and after soaking in  $Cr_2O_7^{2-}$  for 24 h of 1.

# 4. Thermo-gravimetric analysis (TG)



Figure S4. The TG curve of 1 under  $N_2$  atmosphere with a heating rate of 10 °C/min.

# 5. X-ray powder diffraction analysis



Figure S5. PXRD patterns of 1 after the irradiation and soaking in  $Cr_2O_7^{2-}$  anion solution for 24 h.

# 6. Luminescence properties and sensing $Cr_2O_7^{2-}$



Figure S6. The luminescence emission of the original sample and the restored sample.



Figure S7. Luminescence decays of hybrids 1 under ambient conditions.



Figure S8. Comparison of the relative luminescence intensity of  $Cr_2O_7$ <sup>2-</sup> in the presence of mixed anions for 1.



Figure S9. The Stern-Volmer plot of quenched by  $Cr_2O_7^{2-}$  in CH<sub>3</sub>OH. The red line corresponds to a linear fitting result.



Fig S10. The UV-vis absorption spectra of anions and the excitation spectrum of 1.

### 7. XPS for compound 1



Fig. S11 XPS core level spectra of O and N atoms in hybrid 1.



Fig. S12 XPS of hybrid 1.





Fig. S13 EDX analysis of hybrid 1.