Supporting Information for

Encapsulating third donors into D-A hybrid heterostructures to form three-component charge-transfer complexes for enhanced electrical properties

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1. Crystal data and structure refinement for hybrid 1-3

Table 1. Crystallographic Data and Structural Refinements Parameters for hybrid **1-3.**

hybrid	**1**	**2**	**3**
Empirical formula	$C_{16}H_{14}Cu_4I_8N_4S_2$	$C_{32}H_{24}Cu_3I_5N_4S_2$	$C_{36}H_{26}Cu_3I_5N_4S_2$
Formula weight	1595.79	1353.79	1403.85
Temperature/K	293(2)	296.15	296.15
Crystal system	triclinic	orthorhombic	orthorhombic
Space group	*P*-1	*Pnma*	*Pnma*
a/Å	5.9584(3)	15.4744(7)	15.4877(5)
b/Å	11.7691(7)	13.3303(5)	13.3252(4)
c/Å	12.0851(6)	17.5587(8)	18.3914(7)
α/°	110.950(5)	90	90
β/°	97.265(5)	90	90
γ/°	94.237(5)	90	90
Volume/Å^3	778.57(8)	3622.0(3)	3795.6(2)
Z	1	4	4
ρ_{calc}g/cm^3	3.403	2.483	2.457
μ/mm^{-1}	10.775	6.153	5.877
2Θ range for data collection/°	4.148 to 59.164	4.64 to 50.046	4.6 to 50.056
Reflections collected	10094	61691	16565
Independent reflections	3599	3343	3480
Data/restraints/parameters	3599/0/155	3343/0/242	3480/0/267
Goodness-of-fit on F^2	1.027	1.064	1.065
Final R indexes [I>=2σ (I)]	R_1 = 0.0362, wR_2 = 0.0890	R_1 = 0.0678, wR_2 = 0.1499	R1 = 0.0346, wR2 = 0.0536
Final R indexes [all data]	R_1 = 0.0500, wR_2 = 0.0946	R_1 = 0.0776, wR_2 = 0.1572	R1 = 0.0505, wR2 = 0.0599
Largest diff. peak/hole / e Å^{-3}	1.92/-1.78	5.46/-4.10	1.19/-1.26

2 Infrared spectral analyses

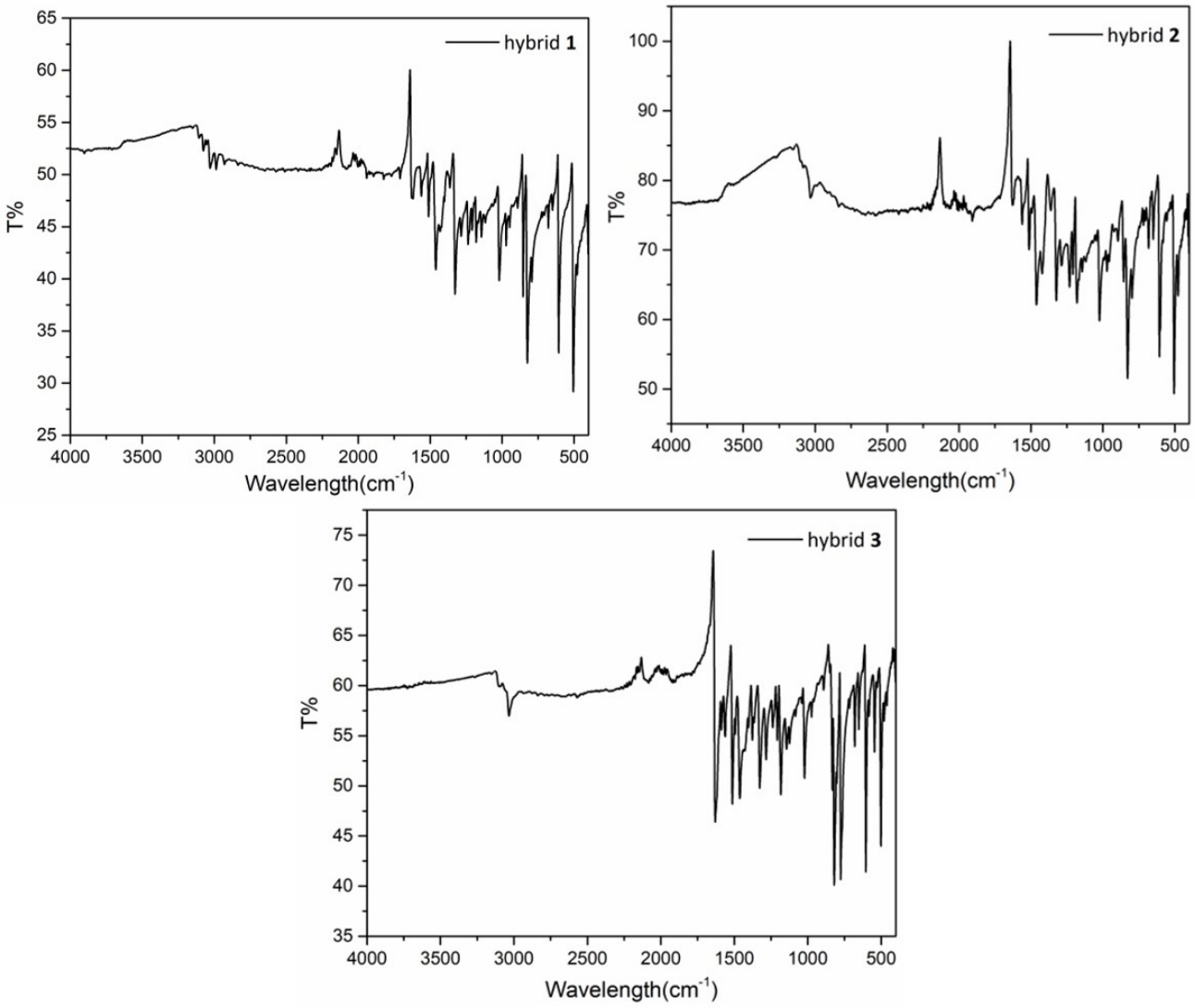

Figure S1. Infrared spectra of hybrids **1-3**.

3. Thermo-gravimetric analyses (TG)

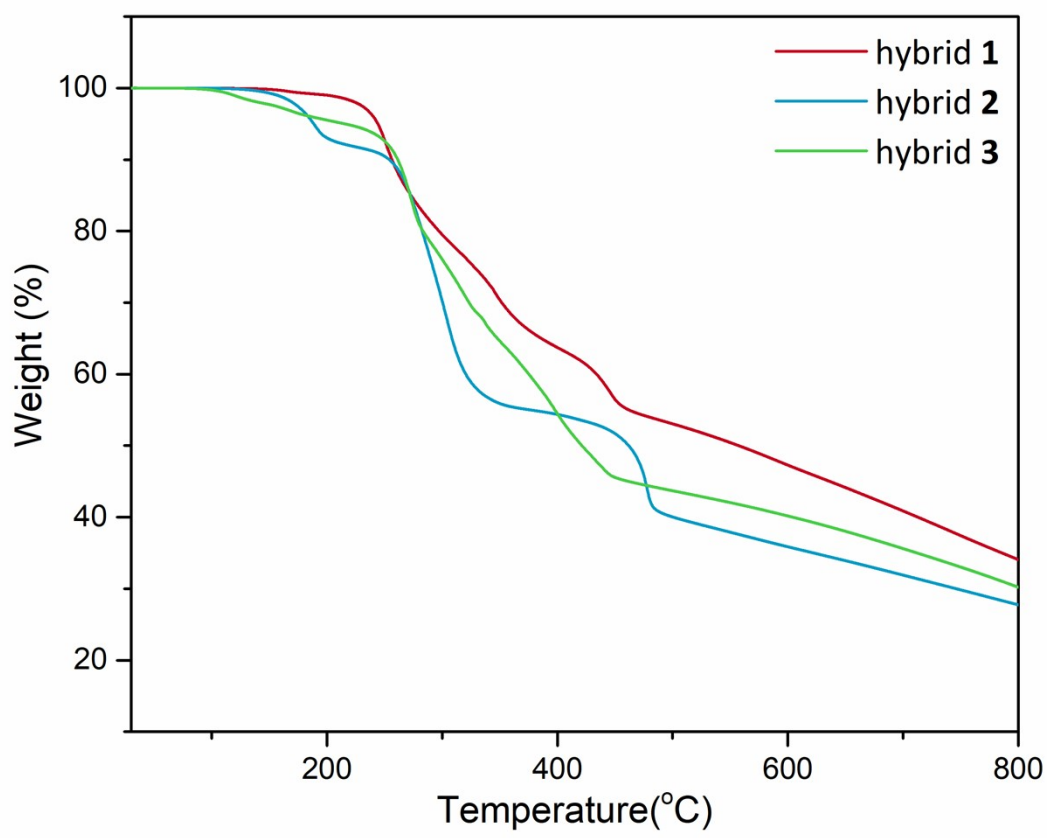

Figure S2. The TG curves of hybrids **1-3** under N_2 atmosphere with a heating rate of 10 °C/min.

4. **UV-Vis absorption measurements**

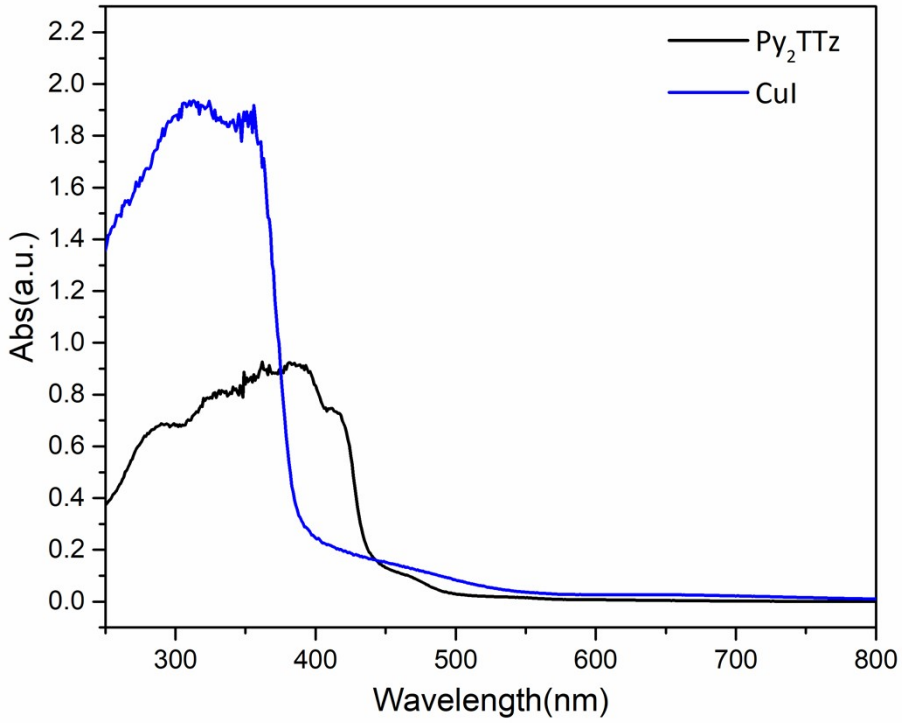

Figure S3. The UV-Vis absorption of CuI and Py_2TTz**.**

5. Energy band gap of hybrids 1-3.

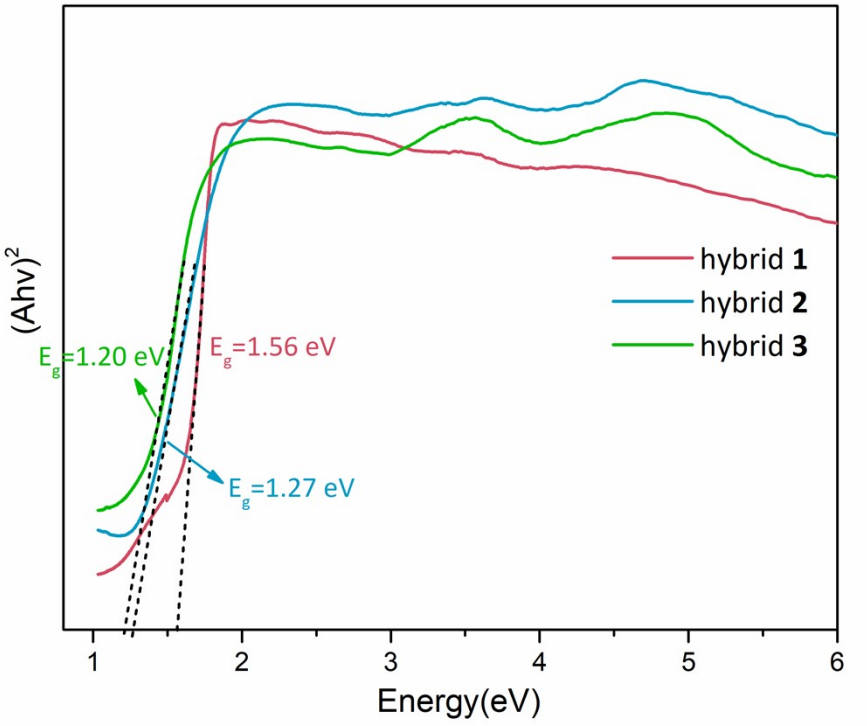

Figure S4. The energy band gap of hybrids **1-3.**