Electronic Supplementary Material (ESI) for CrystEngComm.

Supplementary Information

Photo-sensitive Hybrids Constructed from Diphenyliodonium and Metal-thiocyanates: Photo-induced Structure and Property Transformations

Kai-Yue Song,[a] Zhen-Cong Yang,[a] Pan-Ke Zhou,[a] Lu-Lu Zong,[a] Hao-Hong Li,*[a,b] Rong Jiang,*[a] Zhi-Rong Chen[a,b]

[a]College of Chemistry, Fuzhou University, Fuzhou, Fujian, 350116, P. R. China

[b]Fujian Science & Technology Innovation Laboratory for Optoelectronic Information of China, Fuzhou, Fujian 350108, P. R. China.

Computation Methods

The geometry of DPI radical was simulated using the Gaussian 09 program package.[1] The calculations were performed by using spin restricted DFT wave functions B3LYP. The 6-31g(d) basis set was used for C, H atoms, while CEP-4g basis set was employed for the I atom.

Table S1 Selected bond lengths (Å) and angles (°) for *α*-1 and β-1

***α*-1**					
Mn(1)-N(1)	2.158(4)	Mn(1)-N(2)	2.184(4)	Mn(1)-N(3)	2.155(3)
Mn(1)-N(4)	2.167(4)	Mn(1)-N(5)	2.196(3)	Mn(1)-O(2)	2.382(4)
N(3)-Mn(1)-N(4)	94.48(14)	N(1)-Mn(1)-N(4)	95.73(16)	N(4)-Mn(1)-N(2)	95.33(15)
N(4)-Mn(1)-N(5)	90.24(14)	N(3)-Mn(1)-O(2)	87.56(14)	N(1)-Mn(1)-O(2)	82.68(16)
N(2)-Mn(1)-O(2)	90.84(15)	N(5)-Mn(1)-O(2)	83.52(15)	N(4)-Mn(1)-O(2)	173.58(14)
***β*-1**					
Mn(1)-N(1)	2.160(6)	Mn(1)-N(2)	2.174(6)	Mn(1)-N(3)	2.152(7)
Mn(1)-N(4)	2.172(6)	Mn(1)-N(5)	2.133(7)	Mn(1)-O(1)	2.478(9)
N(5)-Mn(1)-N(3)	96.7(3)	N(5)-Mn(1)-N(1)	95.3(3)	N(5)-Mn(1)-N(4)	96.9(3)
N(5)-Mn(1)-N(2)	91.5(3)	N(3)-Mn(1)-O(1)	81.1(3)	N(1)-Mn(1)-O(1)	87.3(3)
N(4)-Mn(1)-O(1)	88.4(3)	N(2)-Mn(1)-O(1)	83.2(3)	N(5)-Mn(1)-O(1)	174.3(3)

Table S2 Selected bond lengths (Å) and angles (°) for *α*-2 and β-2

***α*-2**					
Ni(1)-S(1)	2.5864(14)	Ni(1)-S(1)#1	2.5864(14)	Ni(1)-N(1)#2	2.057(5)
Ni(1)-N(1)#3	2.057(5)	Ni(1)-N(2)	2.024(5)	Ni(1)-N(2)#1	2.024(5)
N(2)#1-Ni(1)-S(1)#1	87.88(13)	N(2)-Ni(1)-S(1)#1	92.12(13)	N(1)#2-Ni(1)-S(1)#1	88.26(13)
N(1)#3-Ni(1)-S(1)#1	91.74(13)	N(2)#1-Ni(1)-S(1)	92.12(13)	N(2)-Ni(1)-S(1)	87.88(13)

N(1)#2-Ni(1)-S(1)	91.74(13)	N(1)#3-Ni(1)-S(1)	88.26(13)	S(1)#1-Ni(1)-S(1)	180.000(1)
Symmetry code: #1 -x,-y+2,-z+2; #2 -x+1,-y+2,-z+2; #3 x-1,y,z					

***β*-2**

Ni(1)-S(1)	2.6106(16)	Ni(1)-S(1)#1	2.6106(16)	Ni(1)-N(1)	2.025(5)
Ni(1)-N(1)#1	2.025(5)	Ni(1)-N(2)	2.058(5)	Ni(1)-N(2)#1	2.058(5)
N(1)#1-Ni(1)-S(1)#1	88.02(16)	N(1)-Ni(1)-S(1)#1	91.98(16)	N(2)-Ni(1)-S(1)#1	88.31(15)
N(2)#1-Ni(1)-S(1)#1	91.69(15)	N(1)#1-Ni(1)-S(1)	91.98(16)	N(1)-Ni(1)-S(1)	88.02(16)
N(2)-Ni(1)-S(1)	91.69(15)	N(2)#1-Ni(1)-S(1)	88.31(15)	S(1)#1-Ni(1)-S(1)	180.000(1)
Symmetry code: -*x*+1,-*y*+2,-*z*+1					

Table S3 Selected bond lengths (Å) and angles (°) for *α*-3 and β-3

***α*-3**

Cd(1)-S(1)	2.768(3)	Cd(1)-S(4)	2.796(3)	Cd(1)-N(1)	2.393(10)
Cd(1)-N(2)	2.283(8)	Cd(1)-N(3)	2.270(7)	Cd(1)-N(4)	2.308(9)
Cd(2)-S(6)	2.773(3)	Cd(2)-S(6)#1	2.773(3)	Cd(2)-N(5)	2.310(8)
Cd(2)-N(5)#1	2.310(8)	Cd(2)-N(6)#1	2.272(7)	Cd(2)-N(6)	2.272(7)
N(3)-Cd(1)-N(1)	89.8(3)	N(2)-Cd(1)-N(1)	89.0(3)	N(4)-Cd(1)-N(1)	93.8(3)
N(1)-Cd(1)-S(1)	94.0(3)	N(3)-Cd(1)-S(4)	89.8(3)	N(2)-Cd(1)-S(4)	91.5(3)
N(4)-Cd(1)-S(4)	90.8(2)	N(1)-Cd(1)-S(4)	175.4(3)	S(6)-Cd(2)-S(6)#1	180.0
N(6)#1-Cd(2)-S(6)	90.1(3)	N(6)-Cd(2)-S(6)	89.9(3)	N(5)#1-Cd(2)-S(6)	85.9(2)
N(5)-Cd(2)-S(6)	94.1(2)	N(6)#1-Cd(2)-S(6)#1	89.9(3)	N(6)-Cd(2)-S(6)#1	90.1(3)
N(5)#1-Cd(2)-S(6)#1	94.1(2)	N(5)-Cd(2)-S(6)#1	85.9(2)		
Symmetry code: #1 -*x*,-*y*+2,-*z*+1					

***β*-3**

Cd(1)-N(1)	2.166(16)	Cd(1)-N(1)#1	2.166(16)	Cd(1)-N(2)	2.259(9)
Cd(1)-N(2)#1	2.259(9)	Cd(1)-S(1)#2	2.909(5)	Cd(1)-S(1)#3	2.909(5)
N(1)-Cd(1)-S(1)#2	87.2(5)	N(1)#1-Cd(1)-S(1)#2	92.8(5)	N(2)-Cd(1)-S(1)#2	92.5(3)
N(2)#1-Cd(1)-S(1)#2	87.5(3)	N(1)-Cd(1)-S(1)#3	92.8(5)	N(1)#1-Cd(1)-S(1)#3	87.2(5)
N(2)-Cd(1)-S(1)#3	87.5(3)	N(2)#1-Cd(1)-S(1)#3	92.5(3)	S(1)#2-Cd(1)-S(1)#3	180.000(1)
Symmetry code: #1 -*x*+2,-*y*+2,-*z*+1; #2 *x*+1,*y*,*z*; #3 -*x*+1,-*y*+2,-*z*+1					

Table S4 Hydrogen bond details

	D-H	d(H···A)	d(D···A)	∠DHA	Symmetry Code
***α*-1**	O(2)-H(2B)··O(1)	1.86	2.751(4)	145	
***β*-1**	O(1)-H(1B)··O(2)	1.81	2.66(5)	151	
***α*-2**	C(4)-H(4)···S(2)	2.87	3.799(6)	176	1+x,-1+y,z
***β*-2**	C(4)-H(4)···S(2)	2.90	3.827	174	1+x,-1+y,z
***α*-3**	C(4)-H(4)···S(3)	2.84	3.764(15)	175	-x,-1/2+y,1/2-z
***β*-3**	C(2)-H(2)···S(1)	2.87	3.388(13)	117	

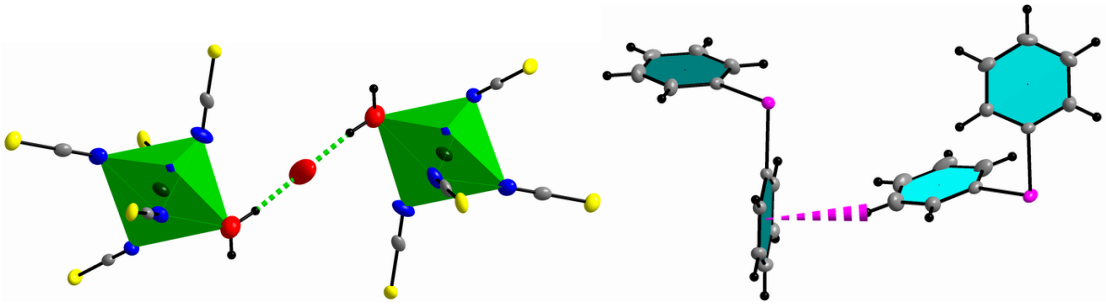
Table S5 C–H···π interaction parameters

	C–H···π	C···C_g/Å	H···C_g/Å	∠(C–H···C_g)/º	Symmetry transformation
***α*-1**	C(3)-H(3)···C_g(1)	3.805(6)	2.93	157	1-x,1-y,1-z
	C_g(1): C(13)→C(14)→C(15)→ C(16)→C(17)→C(18)→				
***β*-1**	C(17)-H(17)···C_g(2)	3.886(15)	2.99	163	2-x,1-y,1-z

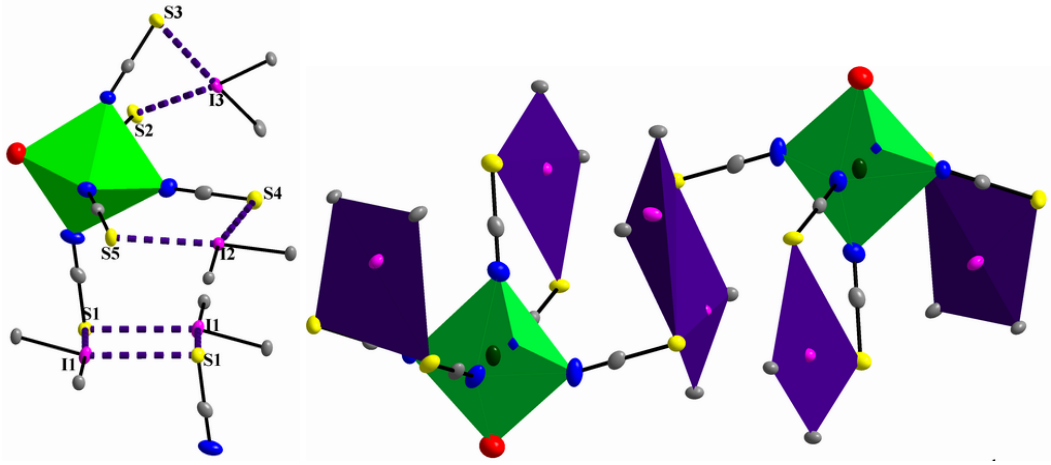
	C_g(1): C(7)→C(8)→C(9)→ C(10)→C(11)→C(12)→				
***α*-2**	C(10)-H(10)···C_g(1)	3.710(7)	2.92	144	3/2-x,1/2+y,1/2-z
	C(12)-H(12)···C_g(1)	3.714(7)	2.80	168	-1+x,y,z
	C_g(1): C(1)→C(2)→C(3)→ C(4)→C(5)→C(6)→				
***β*-2**	C(8)-H(8)···C_g(1)	3.766(8)	2.84	171	-1+x,y,z
	C_g(1): C(1)→C(2)→C(3)→ C(4)→C(5)→C(6)→				
***α*-3**	C(12)-H(12)···C_g(1)	3.869(13)	2.95	172	
	C_g(1): C(13)→C(14)→C(15)→ C(16)→C(17)→C(18)→				
	C(28)-H(28)···C_g(2)	3.774(16)	2.97	145	-1-x,-1/2+y,1/2-z
	C_g(2): C(19)→C(20)→C(21)→ C(22)→C(23)→C(24)→				
	C(30)-H(30)···C_g(3)	3.790(15)	2.86	175	-1+x,y,z
	C_g(3): C(1)→C(2)→C(3)→ C(4)→C(5)→C(6)→				
***β*-3**	C(8)–H(8)···C_g(1)	3.907(14)	2.99	170	1+x,y,z
	C_g(1): C(1)→C(2)→C(3)→ C(4)→C(5)→C(6)→				

Table S6 Secondary hypervalent I(III)···S interactions (lengths in Å)

***α*-1**		***β*-1**	
I(1)···S(1)	3.249	I(1)···S(2)#1	3.192
I(1)···S(1)#1	3.340	I(1)···S(5)#1	3.289
I(2)··· S(4)	3.267	I(2)··· S(3	3.355
I(2)···S(5)	3.173	I(2)···S(3)#1	3.299
I(3)···S(2)	3.297	I(3)···S(1)	3.269
I(3)···S(3)	3.227	I(3)···S(4)	3.347
Symmetry Code: #1: 1-*x*,1-*y*,1-*z*			
***α*-2**		***β*-2**	
I(1)···S(1)#1	3.385	I(1)···S(1)	3.410
I(1)···S(2)#2	3.159	I(1)···S(2)#3	3.176
Symmetry Code: #1: 1/2-*x*,-1/2+*y*,3/2-*z*; #2: -1/2+*x*,3/2-*y*,-1/2+*z*; #3: -*x*,2-*y*,1-*z*			
***α*-3**		***β*-3**	
I(1)···S(4)#1	3.411	I(1) ···S(1)	3.416
I(1)···S(5)#1	3.200	I(1) ···S(2)	3.193
I(2)···S(2)	3.188		
I(2)···S(6)	3.523		
I(3)···S(3)#2	3.171		
Symmetry Code: #1: -*x*,2-*y*,1-*z*; #2: -1-*x*,2-*y*,1-*z*			

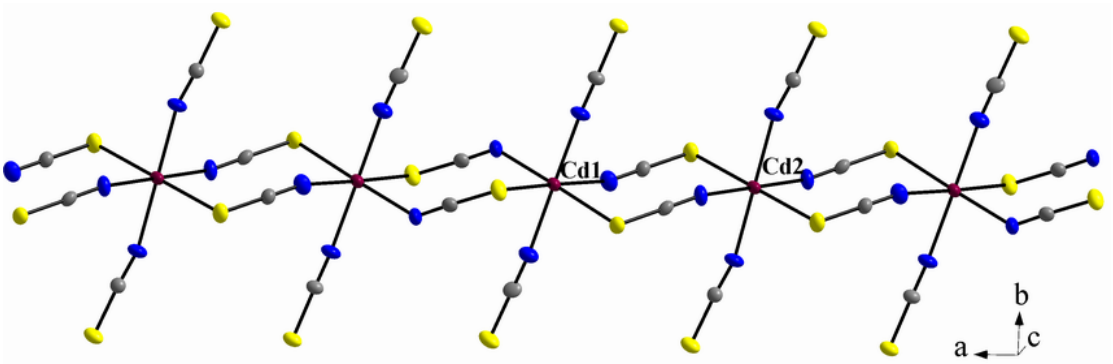


(a) (b)

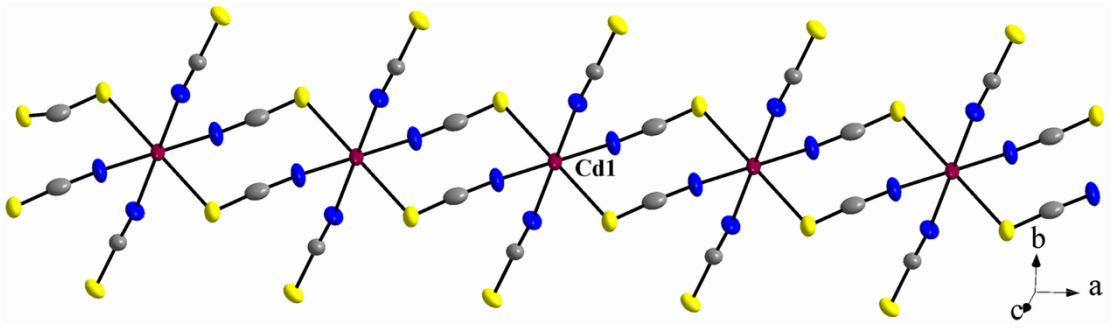


(c) (d)

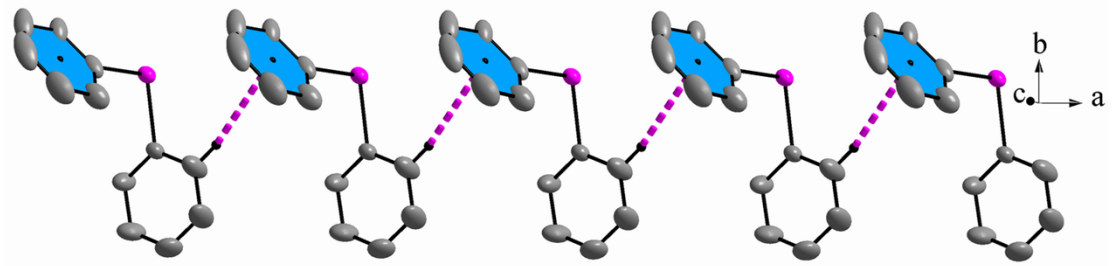
Fig. S1 (a) {$[Mn(SCN)_5(H_2O)]_2^{6-}\cdot H_2O$} dimer based on O-H···O hydrogen bond; (b) DPI^+ dimmer based on C–H···π interaction of *α*-1; (c)the structure of $(DPI)_3[Mn(SCN)_5(H_2O)]$ based on the secondary I(III)···S contacts in *α*-1; (d) $(DPI)_3[Mn(SCN)_5(H_2O)]$ dimer based on bridged DPI^+ in *α*-1 (other C and H atoms on benzene rings were omitted for clarity, green: MnN_5O octahedron, purple: IS_2C_2 planar square)



(a)

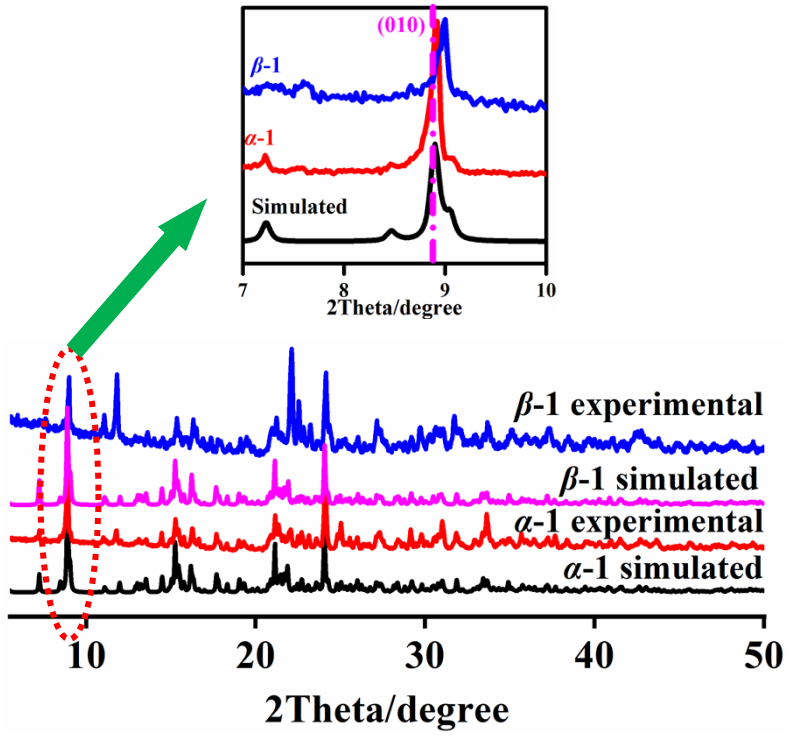


(b)

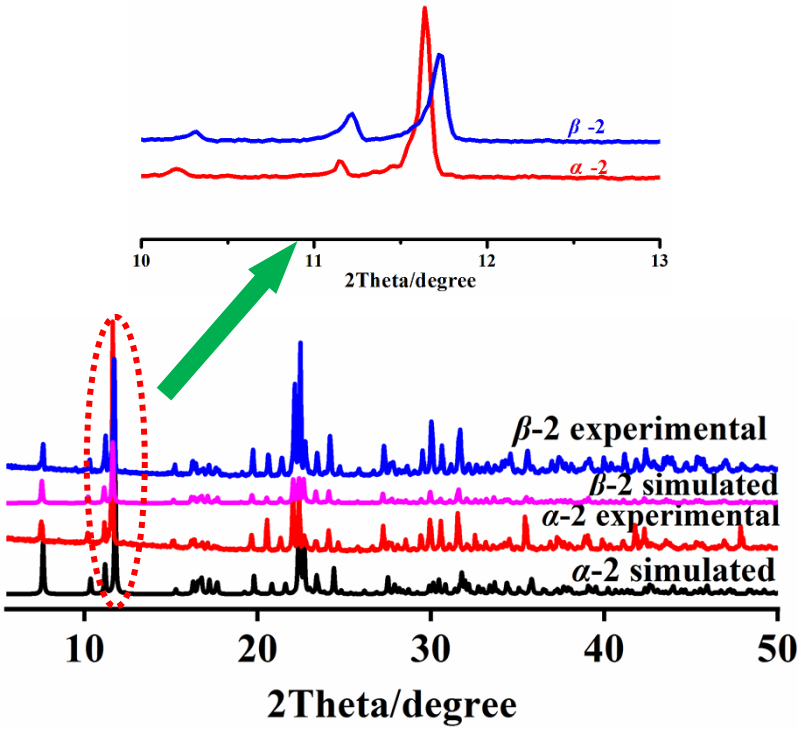


(c)

Fig. S2 (a) 1-D zigzag $\{[Cd(SCN)_4]_3^{6-}\}_n$ anionic chain of α-3; (b) 1-D $\{[Cd(SCN)_4]^{2-}\}_n$ of β-3; (c) 1-D $(DPI)_n^{n+}$ chain based on C–H···π interaction in β-3



(a)



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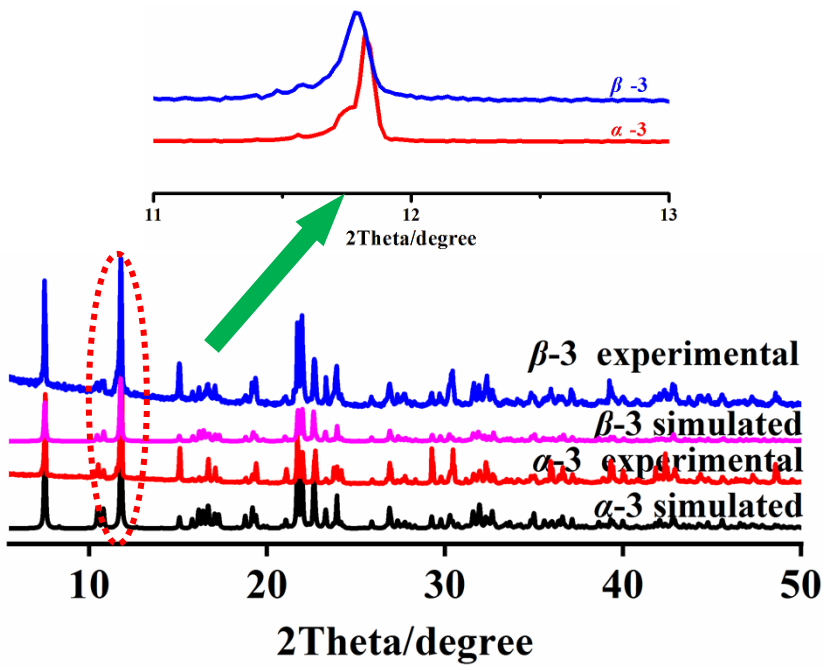
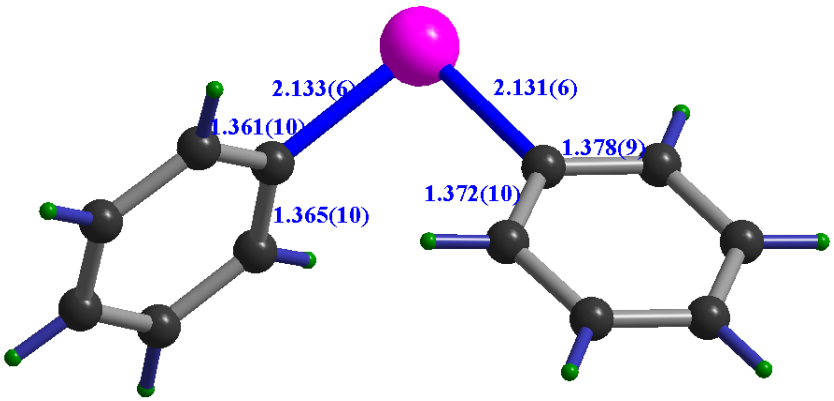
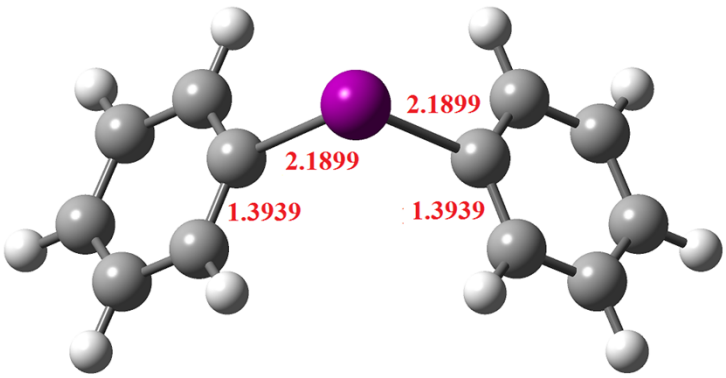


(c)

Fig. S3 Powder X-ray diffraction (PXRD) patterns of three hybrids before and after irradiating: (a) 1; (b) 2; (c) 3

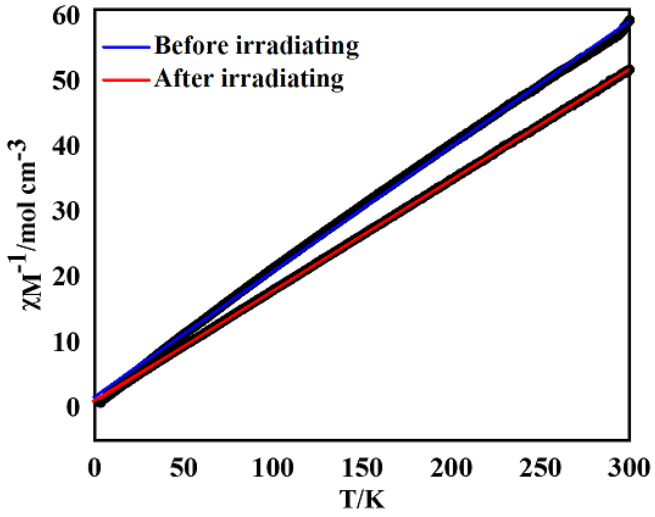


(a)



(b)

Fig. S4 The geometry of DPI^+ cation: (a) in *β*-2; (b) the calculated model based on DFT calculation



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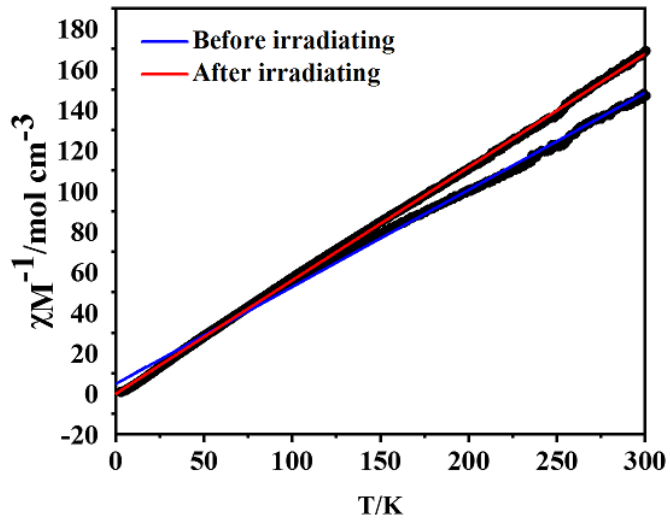

(b)

Fig. S5 The $1/\chi_M$ vs. T plots: (a) *α*-1; (b) *α*-2. The red and blue lines represent the fits

References

1 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, Jr. J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth,

P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian 09, Revision A01, Gaussian, Inc., Wallingford, CT, 2009.