Electronic Supplementary Information

Luminescence mechanochromism of copper iodide clusters: a rational investigation

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Table S1. Crystal data of **1a** and **1b** $[Cu_4I_4(PPh_3)_4]$ at 300 K.

Polymorph	**1a** [1]	**1b**
Space group	Monoclinic $P2_1/c$	Cubic $I\bar{4}3d$
Cell parameters (Å, °)	*a* 13.5413(10) *b* 26.949(2) *c* 19.4847(14) *β* 99.022(1)	30.1722(3)
Cell volume (Å³)	7022.5(7)	27467.6(8)
Cu-Cu (Å)	2.840(1) 2.868(1) 2.897(1) 2.928(1) 3.108(1) 3.166(1)	2.953(2) x3 3.185(2) x3
mean	*2.968(1)*	*3.069(2)*
Cu-I (Å)	22.6620(8) 2.6909(9) 2.7078(8) 2.6547(9) 2.6973(9) 2.7195(9) 2.6704(9) 2.6892(9) 2.7353(9) 2.6700(9) 2.7057(8) 2.7141(9)	2.6259(10) x3 2.7170(7) x3 2.8016(11) x3 2.6820(11) x3
mean	*2.693(1)*	*2.707(1)*
Cu-P (Å)	2.253(2) 2.258(2) 2.252(2) 2.261(2)	2.252(2) x3 2.267(3) x1
mean	*2.256(2)*	*2.256(3)*
I-Cu-I (°)	102.98(3) 103.21(3) 103.65(3) 105.47(3) 107.81(3) 108.83(3) 108.47(3) 108.85(3) 112.01(3) 113.13(3) 114.93(3) 115.07(3)	104.67(3) x3 104.80(3) x3 107.48(3) x3 112.84(3) x3
mean	*108.70(3)*	*107.45(3)*

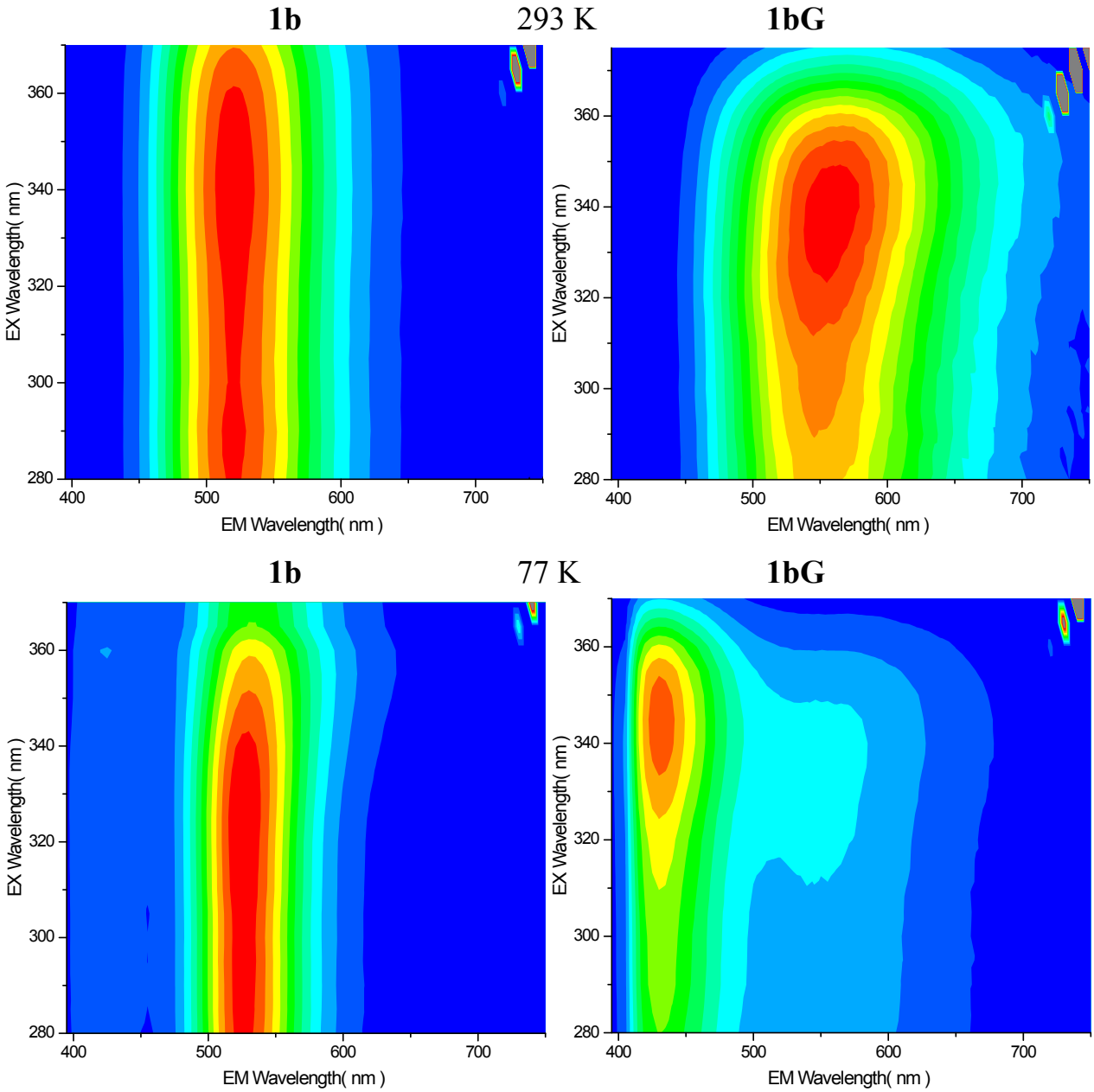

Figure S1. Solid-state photoluminescence maps (excitation *vs*. emission) of **1b** and **1bG** at 293 and 77K.

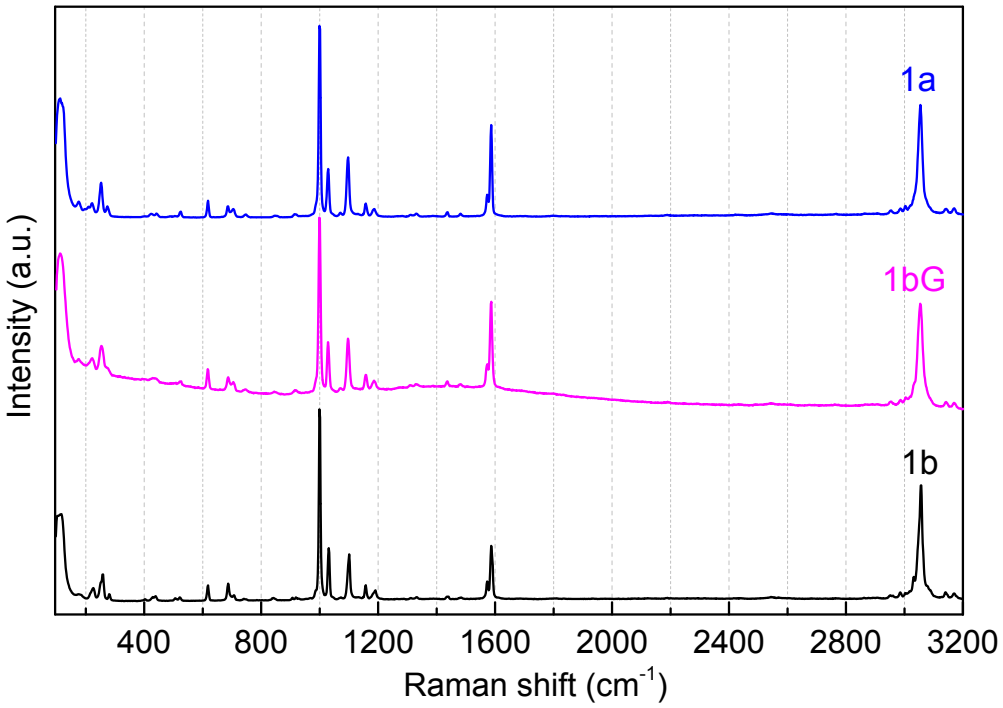

Figure S2. Raman spectra of **1b** before and after grinding (**1bG**) and of **1a** for comparison.

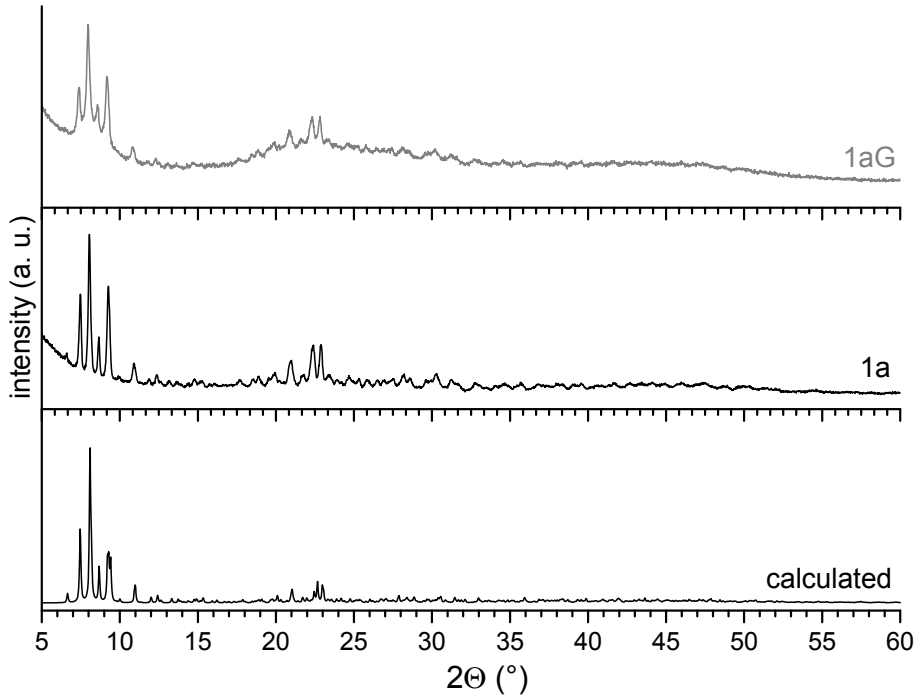

Figure S3. PXRD of cluster **1a** before and after grinding (**1aG**) and calculated pattern from SCXRD data.

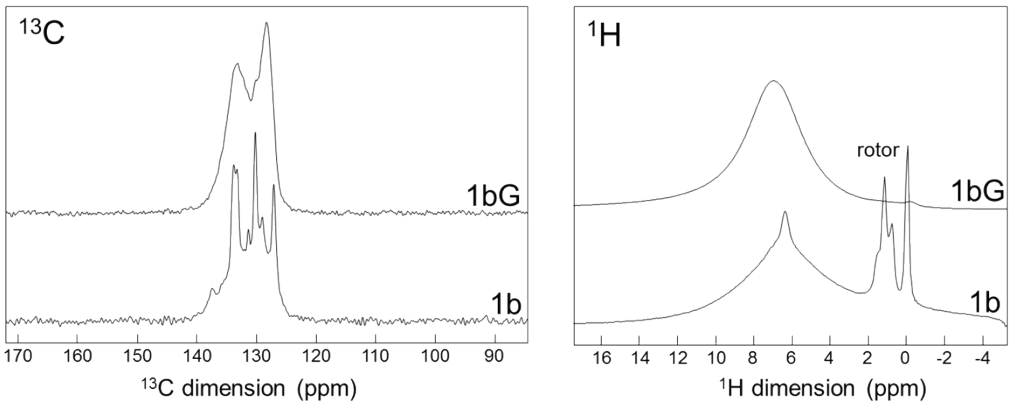

Figure S4. ^{1}H and ^{13}C Solid state NMR spectra of **1b** before and after grinding (**1bG**).

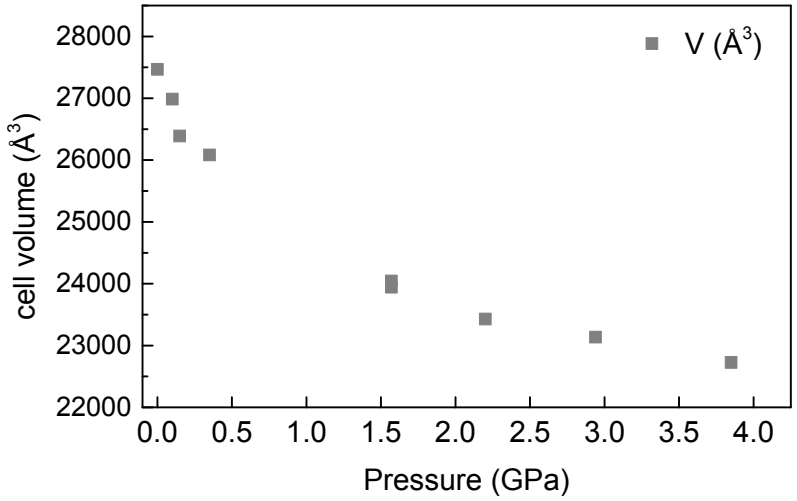

Figure S5. Pressure dependence of cell volume determined from SCXRD analysis of **1b**.

Table S2. Photoluminescence data of $[Cu_4I_4(PPh_3)_4]$ **1**. Lifetimes and quantum yields have been measured at 293 K.

	λ_{max} (nm)		Lifetime	Quantum Yield
	293 K	77 K	τ (μs)	QY (%)
1a	545	415 587	6.0	64
1b	520	420 540	3.2	88
1bG	560	430 560	0.4 (14 %) 2.9 (86 %)	44

Table S3. Crystal data and structure refinement for $[Cu_4I_4(PPh_3)_4]$ ($C_{72}H_{60}Cu_4I_4P_4$) at different pressures at 293 K.

Pressure (GPa)	**0 out of the DAC** (300 K)	**0.1**	**0.15**	**0.35**	**1.57**	**1.57**	**2.2**	**2.94**	**3.85**
CCDC n°	1903858	1903859	1903860	1903861	1903862	1903863	1903864	1903865	1903866
Molecular weight	1810.84	1810.84	1810.84	1810.84	1810.84	1810.84	1810.84	1810.84	1810.84
Crystal system	cubic	cubic	cubic	cubic	cubic	tetragonal	tetragonal	tetragonal	tetragonal
Space group	$I\bar{4}3d$	$I\bar{4}3d$	$I\bar{4}3d$	$I\bar{4}3d$	$I\bar{4}3d$	$I\bar{4}2d$	$I\bar{4}2d$	$I\bar{4}2d$	$I\bar{4}2d$
a/Å	30.1722(3)	29.9951(15)	29.7722(18)	29.6561(15)	28.863(2)	28.798(9)	28.590(9)	28.449(15)	28.308(11)
b/Å						28.798(9)	28.590(9)	28.449(15)	28.308(11)
c/Å						28.868(5)	28.661(5)	28.584(16)	28.359(8)
α/°	90	90	90	90	90	90	90	90	90
β/°	90	90	90	90	90	90	90	90	90
γ/°	90	90	90	90	90	90	90	90	90
Volume/Å^3	27467.6(8)	26987(4)	26390(5)	26082(4)	24044(6)	23942(15)	23427(15)	23135(28)	22726(19)
Z	16	16	16	16	16	16	16	16	16
ρ_{calc}mg/mm^3	1.752	1.783	1.823	1.894	2.001	2.010	2.054	2.080	2.117
μ /mm^{-1}	3.154	3.210	3.283	3.324	3.603	3.618	3.698	3.745	3.812
F(000)	14080.0	14080.0	14080.0	14464.0	14080.0	14080.0	14080.0	14080.0	14080.0
Crystal size/mm^3	0.15 × 0.1 × 0.08	0.06 × 0.05 × 0.03	0.06 × 0.05 × 0.03	0.06 × 0.05 × 0.03	0.06 × 0.05 × 0.03	0.06 × 0.05 × 0.03	0.06 × 0.05 × 0.03	0.06 × 0.05 × 0.03	0.06 × 0.05 × 0.03
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range	6.886 to 52.736	3.326 to 52.262	4.326 to 52.066	3.884 to 52.076	4.462 to 49.404	4 to 49.384	4.03 to 46.426	4.526 to 46.51	4.55 to 46.51
Reflexions collected	25045	4461	4562	4547	4207	4458	3884	4195	4688
Independent reflexions	4690 [R_{int} = 0.0365, R_{sigma} = 0.0259]	2214 [R_{int} = 0.0447, R_{sigma} = 0.0646]	2194 [R_{int} = 0.0502, R_{sigma} = 0.0647]	2185 [R_{int} = 0.0566, R_{sigma} = 0.0803]	2019 [R_{int} = 0.0698, R_{sigma} = 0.0866]	3053 [R_{int} = 0.0602, R_{sigma} = 0.0976]	2722 [R_{int} = 0.0891, R_{sigma} = 0.1372]	2836 [R_{int} = 0.0956, R_{sigma} = 0.1428]	3078 [R_{int} = 0.1352, R_{sigma} = 0.1807]
Data/restraints/param.	4690/0/253	2214/0/253	2194/0/253	2185/0/253	2019/24/128	3053/0/372	2722/0/253	2836/54/198	3078/75/243
GOF on F^2	1.105	1.079	1.079	1.060	1.077	1.085	1.061	1.037	1.061

R_1/wR_2 (I>=2σ (I))	0.0293/0.0537	0.0481/0.0994	0.0445/0.0907	0.0483/0.0958	0.0618/0.1361	0.0598/0.1366	0.0821/0.1960	0.1010/0.2499	0.1239/0.2962
R_1/wR_2 (all)	0.0367/0.0564	0.0563/0.1058	0.0560/0.0995	0.0611/0.1090	0.0812/0.158	0.0795/0.1571	0.1088/0.2290	0.1246/0.2874	0.1651/0.3506
Largest diff. peak/hole / eÅ^{-3}	0.36/-0.29	0.79/-0.46	0.63/-0.48	0.74/-0.46	1.29/-0.99	1.21/-0.77	1.37/-1.11	1.72/-1.71	1.91/-1.31

Table S4. Selected intra-molecular bond lengths (Å) and angles (°) of $[Cu_4I_4(PPh_3)_4]$ **1b** at different pressures from SCXRD experiment at 293 K.

Pressure GPa	**0 out of DAC**	**0.1**	**0.15**	**0.35**	**1.57**	**1.57**	**2.2**	**2.94**	**3.85**
Cu1-Cu1	2.953(2) x3	2.923(4) x3	2.892(3) x3	2.857(4) x3	2.742(5) x3	2.728(6)	2.679(8)	2.663(10)	2.625(13)
Cu1-Cu4	3.185(2) x3	3.152(4) x3	3.121(3) x3	3.077(4) x3	2.918(5) x3	2.751(6)	2.719(8)	2.698(10)	2.652(17)
						2.756(8)	2.719(11)	2.698(13)	2.655(13)
						2.910(9)	2.873(11)	2.832(13)	2.820(18)
						2.920(6)	2.890(8)	2.856(9)	2.844(11)
						2.922(5)	2.897(8)	2.876(10)	2.855(13)
mean	*3.069(2)*	*3.038(4)*	*3.007(3)*	*2.967(4)*	*2.830(5)*	*2.831(9)*	*2.796(11)*	*2.771(13)*	*2.742(17)*
Cu1-I3	2.802(1) x3	2.804(3) x3	2.706(2) x3	2.684(3) x3	2.691(2) x3	2.563(4)	2.686(7)	2.685(8)	2.561(13)
Cu1-I3	2.626(1) x3	2.619(2) x3	2.604(2) x3	2.811(3) x3	2.566(3) x3	2.699(6)	2.817(10)	2.840(12)	2.695(9)
Cu1-I1	2.682(1) x3	2.686(3) x3	2.796(2) x3	2.7167(19)x3	2.790(4) x3	2.777(5)	2.553(8)	2.539(9)	2.805(9)
Cu4-I3	2.717(1) x3	2.720(2) x3	2.673(2) x3	2.611(2) x3	2.666(4) x3	2.682(4)	2.686(6)	2.690(7)	2.566(9)
						2.575(6)	2.577(9)	2.561(10)	2.794(9)
						2.782(5)	2.790(7)	2.795(8)	2.695(13)
						2.801(8)	2.710(8)	2.703(10)	2.832(15)
						2.689(5)	2.560(6)	2.558(7)	2.684(11)
						2.564(6)	2.776(6)	2.771(8)	2.552(12)
						2.655(5)	2.638(7)	2.632(8)	2.603(10)
						2.662(4)	2.653(6)	2.668(11)	2.650(9)
						2.677(7)	2.660(10)	2.664(7)	2.631(15)
mean	*2.707(1)*	*2.707(3)*	*2.695(2)*	*2.706(3)*	*2.678(4)*	*2.677(8)*	*2.676(10)*	*2.676(12)*	*2.672(15)*
Cu1-P1	2.252(2) x3	2.255(4) x3	2.247(4) x3	2.254(5) x3	2.243(6) x3	2.229(9)	2.213(12)	2.236(14)	2.250(18)
Cu4-P4	2.267(3) x1	2.272(7) x1	2.259(7) x1	2.270(8) x1	2.262(12) x1	2.249(11)	2.230(14)	2.216(17)	2.21(2)
Cu2-P2						2.240(8)	2.239(11)	2.245(13)	2.246(17)

Cu3-P3						2.266(16)	2.280(20)	2.29(3)	2.32(3)
mean	*2.256(2)*	*2.259(7)*	*2.250(7)*	*2.258(8)*	*2.248(12)*	*2.246(16)*	*2.241(20)*	*2.25(2)*	*2.26(3)*
I-Cu-I	104.67(3) x3	105.17(8)x3	105.50(8) x3	106.50(9) x3	108.55(11)x3	109.25(19)	108.60(19)	108.9(2)	109.3(4)
	104.80(3) x3	105.60(8)x3	105.80(8) x3	106.76(9) x3	109.28(14)x3	116.3(2)	109.1(2)	110.0(2)	119.2(5)
	112.84(3) x3	113.46(9)x3	113.90(8) x3	114.76(9) x3	116.29(13)x3	109.25(17)	109.3(3)	109.7(4)	109.5(4)
	107.48(3) x3	107.77(8)x3	107.95(7) x3	108.49(8) x3	109.07(11)x3	108.8(2)	109.6(3)	109.6(3)	111.0(4)
						108.24(14)	117.3(3)	117.7(3)	117.5(4)
						108.61(16)	109.1(2)	109.2(3)	109.9(3)
						109.6(2)	110.5(3)	111.5(3)	110.0(5)
						116.0(2)	116.3(3)	116.8(3)	109.4(3)
						109.13(14)	109.75(19)	109.6(2)	110.0(3)
						108.93(18)	109.45(2)	110.0(3)	110.0(4)
						116.18(17)	116.9(2)	117.8(3)	117.9(4)
						108.8(2)	109.2(3)	109.0(4)	110.1(4)
mean	*107.45(3)*	*108.00(9)*	*108.29(8)*	*109.13(9)*	*110.80(14)*	*110.76(20)*	*111.3(3)*	*111.7(4)*	*112.0(5)*

References

[1] H. Kitagawa, Y. Ozawa, K. Toriumi, *Chem. Commun*. **2010**, *46*, 6302.