Supporting Information for

Cd(II)-Coordination Framework: Synthesis, Anion-Induced Structural Transformation, Anion-Responsive Luminescence and Anion Separation

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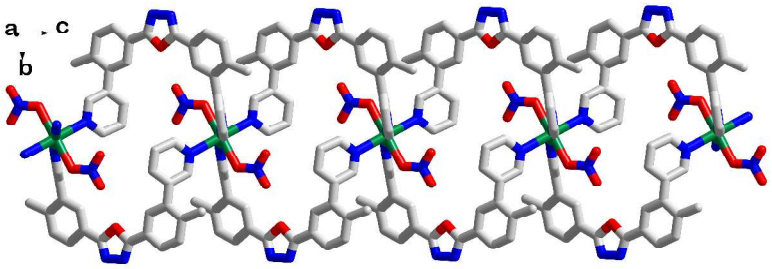


Figure S1. 1D bimetallic ring-containing chain of **1**.

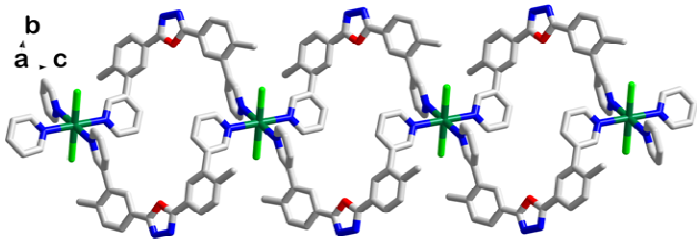


Figure S2. 1D bimetallic ring-containing chain of **2**.

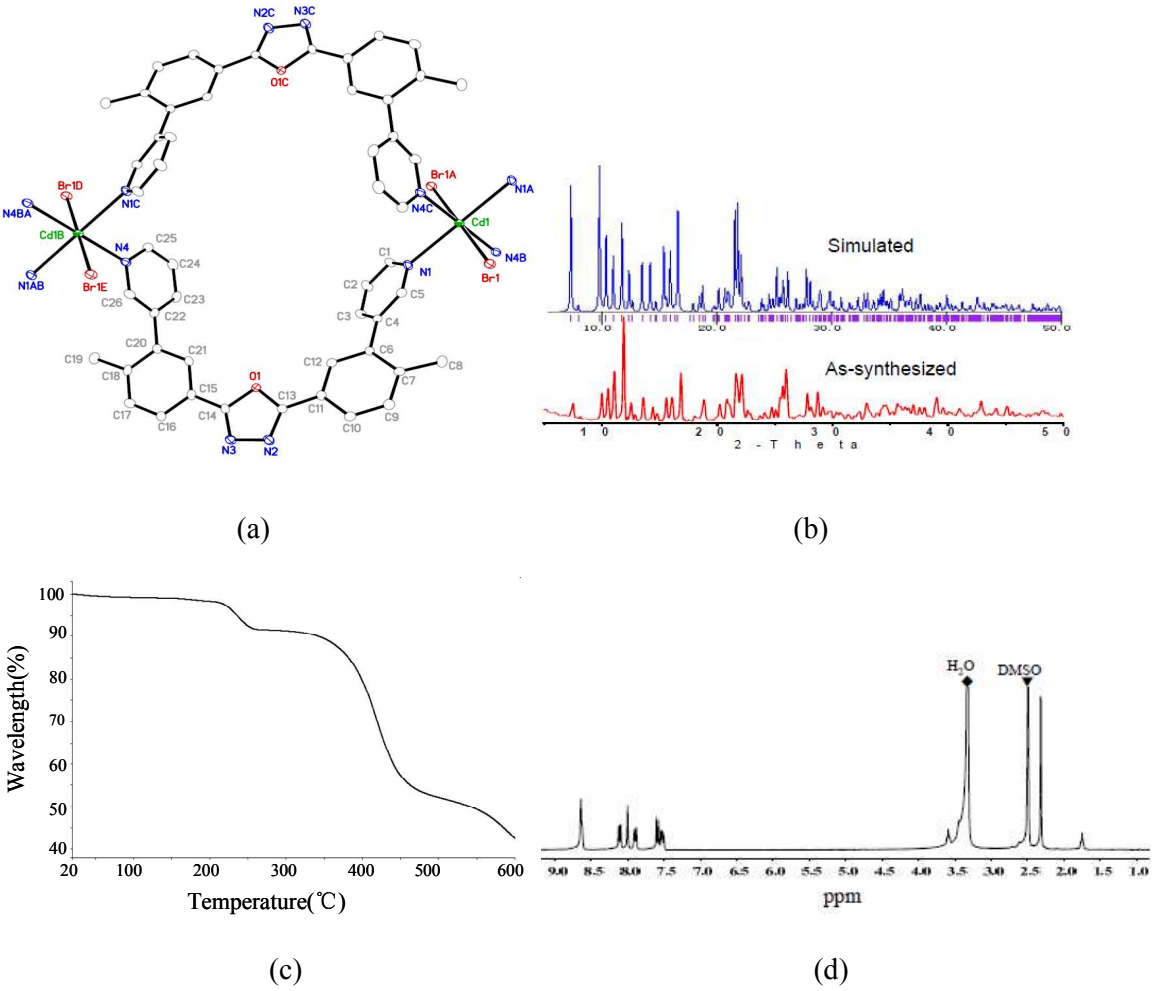
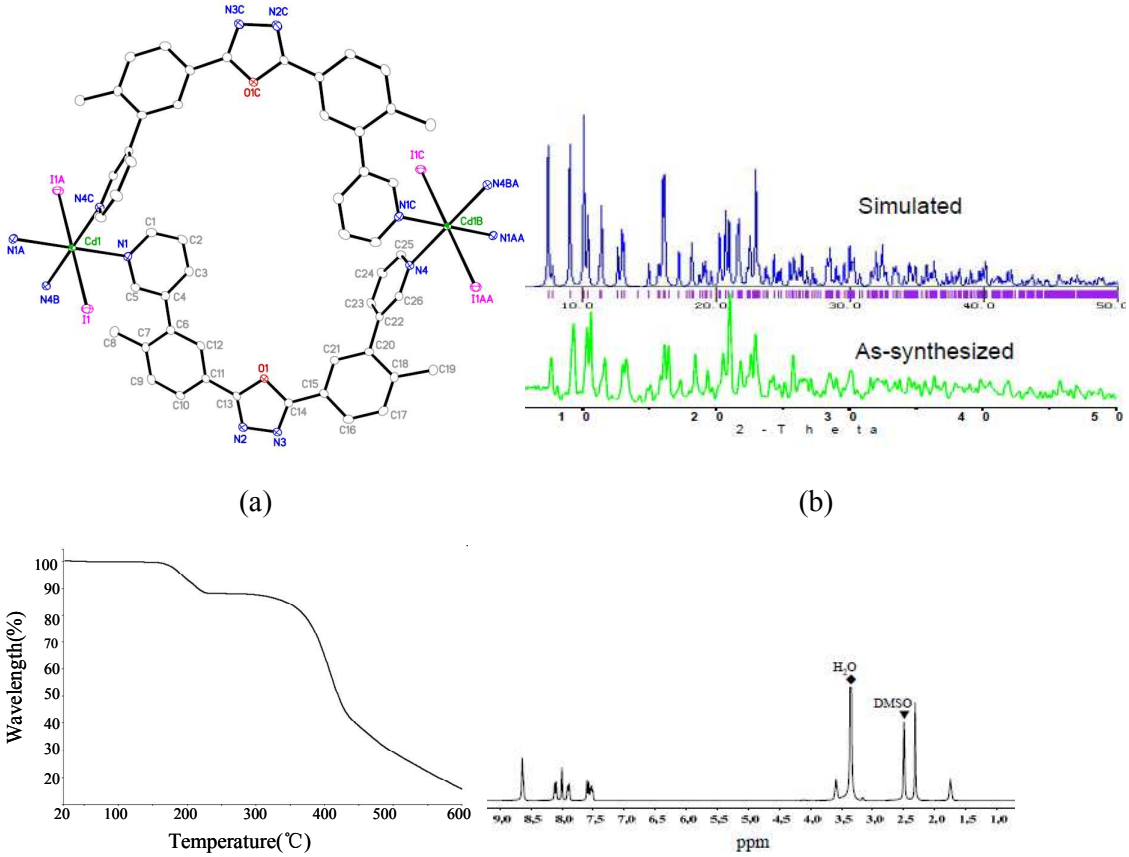


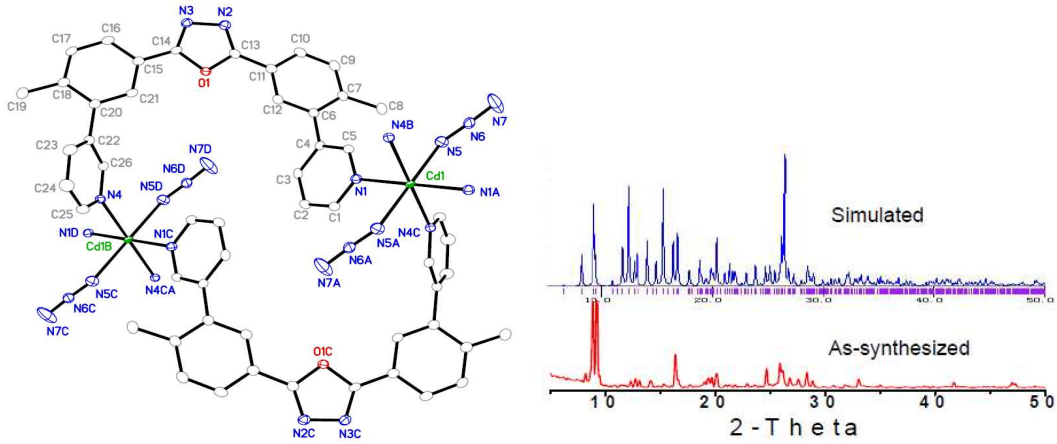
Figure S3. Compound **3** ($Cd\mathbf{L}_2Br_2{\cdot}2(C_4H_8O)$): (a) ORTEP figure. (b) XRPD patterns. (c) TGA trace (observed and calculated THF weight losses are 6.3 and 6.8 %, respectively). (d) ^{1}H NMR spectrum.



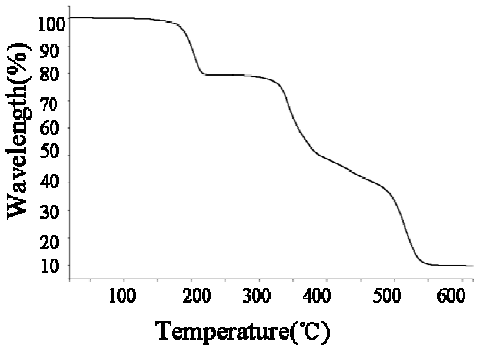
(a) (b)

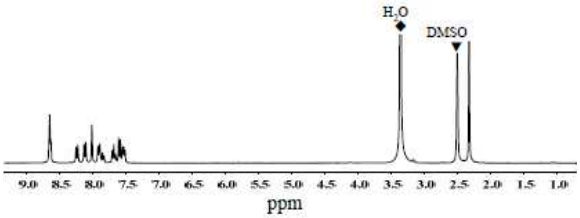
(c) (d)

Figure S4. Compound **4** ($Cd\mathbf{L}_2I_2{\cdot}2(C_4H_8O)$): (a) ORTEP figure. (b) XRPD patterns. (c) TGA trace (observed and calculated THF weight losses are 10.9 and 11.6 %, respectively). (d) ^1H NMR spectrum.



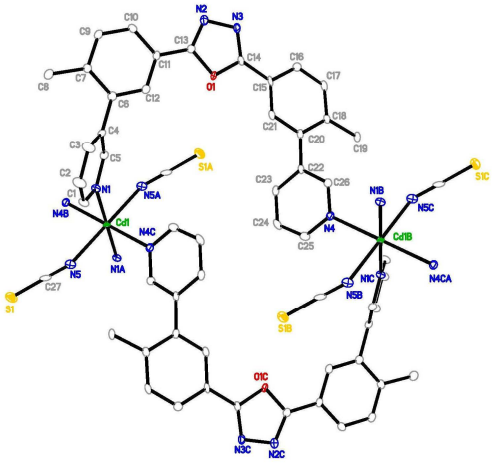
(a) (b)

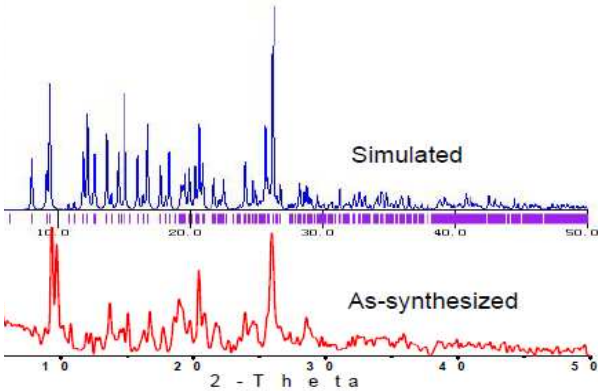




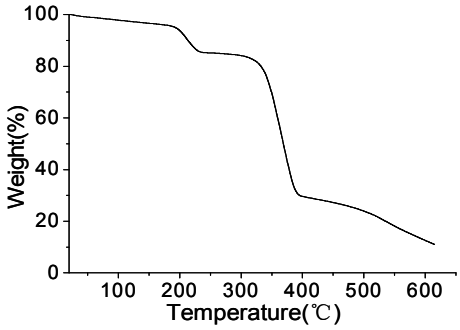
(c) (d)

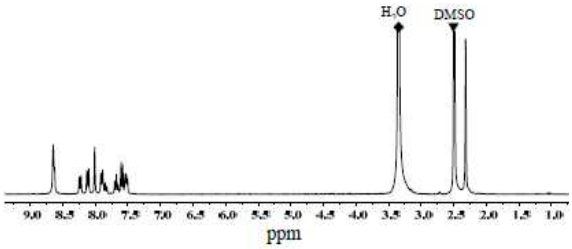
Figure S5. Compound **5** ($CdL_2(N_3)_2{\cdot}2(C_6H_5NO_2)$): (a) ORTEP figure. (b) XRPD patterns. (c) TGA trace (observed and calculated $C_6H_5NO_2$ weight losses are 19.7 and 20.8 %, respectively). (d) ^{1}H NMR spectrum.





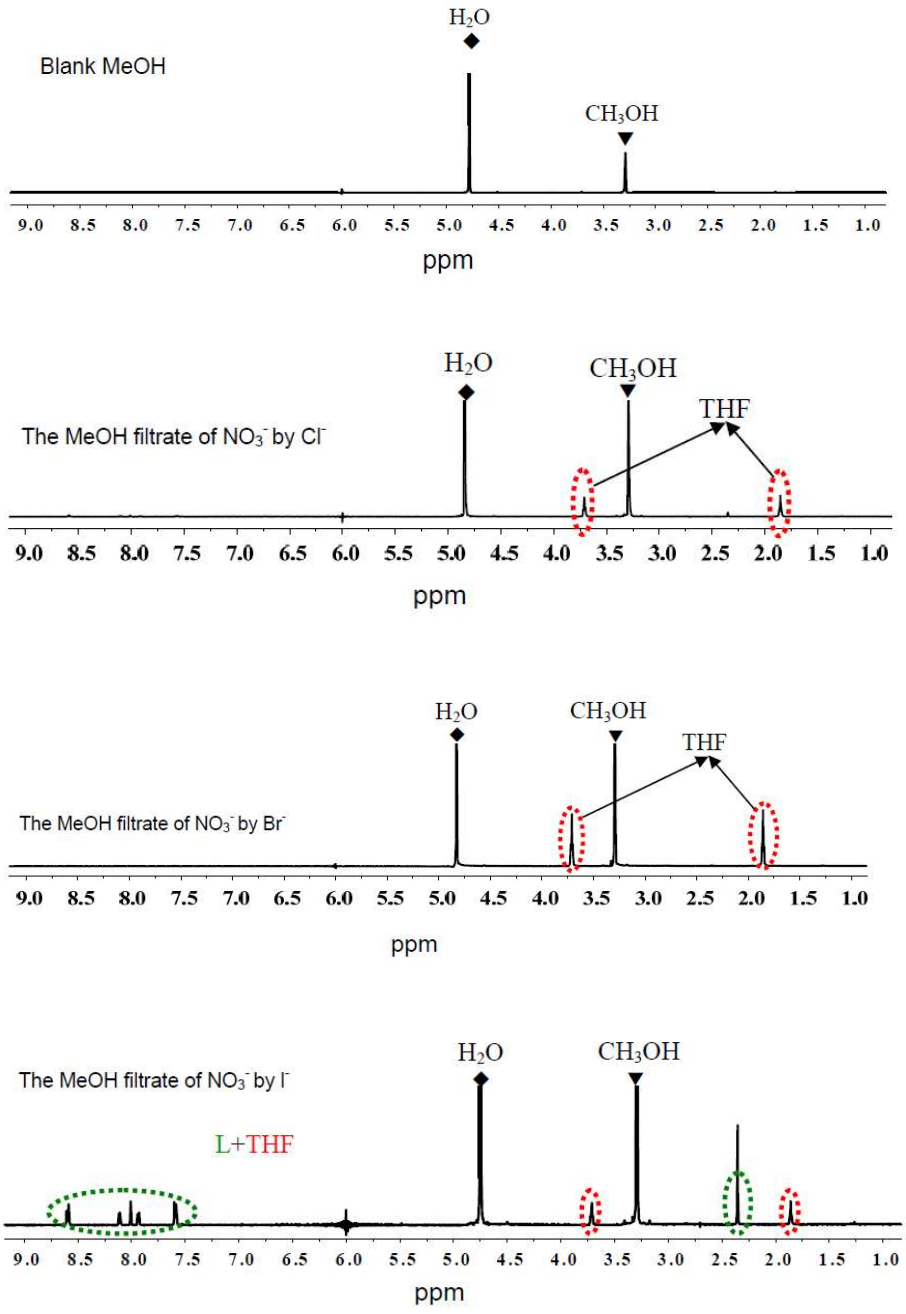
(a) (b)





(c) (d)

Figure S6. Compound **6** ($Cd\mathbf{L}_2(SCN)_2 \cdot 2(C_6H_5NO_2)$): (a) ORTEP figure. (b) XRPD patterns. (c) TGA trace (observed and calculated $C_6H_5NO_2$ weight losses are 19.2 and 14.7 %, respectively). (d) ^{1}H NMR spectrum.



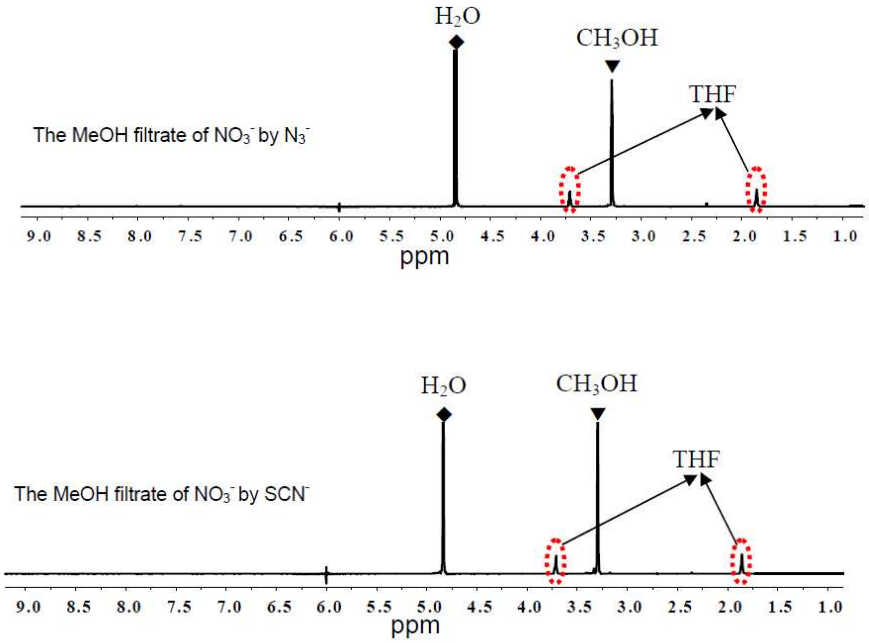


Figure S7. ^{1}H NMR spectra on blank MeOH and MeOH filtrates which were obtained after NO_3^- in **4** replaced by X^- (X = Cl^-, Br^-, I^-, N_3^- and SCN^-). Except NO_3^- by I^-, no ligand signals were detected in their filtrates, which indicates these compounds are insoluble in MeOH, so the possibility of a dissolution-recrystallization mechanism for explaining such an anion-exchange reaction is impossible.

Table S1. Formation energies[1] of Cd(II)-heteroatom.[a]

	$\triangle E$(KJ/mol)
NO_3^--CdN_4^{2+}	-189.9
Cl^--CdN_4^{2+}	-212.0
Br^--CdN_4^{2+}	-277.5
N_3^--CdN_4^{2+}	-282.8
SCN^--CdN_4^{2+}	-161.5

[a] We have extracted the model of the complexes from relevant X-ray crystallographic data. B3LYP/6-31G was used to calculate the formation energies of different coordination bonds. Density functional theory (DFT) calculations were performed with the Gaussian 03[2] packages. I-Cd formation energy was not provided because the replacement of NO_3^- by I^- is a dissolution-reaction-recrystallization process. As shown in Table S1, the calculated formation energies are basically in accord with the obtained results.

Reference

1. (a) Vázquez, M.-V.; Martínez, A. *J. Phys. Chem. A.* **2007**, *111*, 9931. (b) Lee, E. P. F.; Soldán, P.; Wright, T. G. *J. Phys. Chem. A* **2001**, *105*, 8510.

2. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A. Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A. P.; Salvador, Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03, Gaussian Inc.*, Pittsburgh, PA, 2003.