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Precise Control and Consecutive Modulation of Spin Transition Temperature Using Chemical Migration in Porous Coordination Polymers

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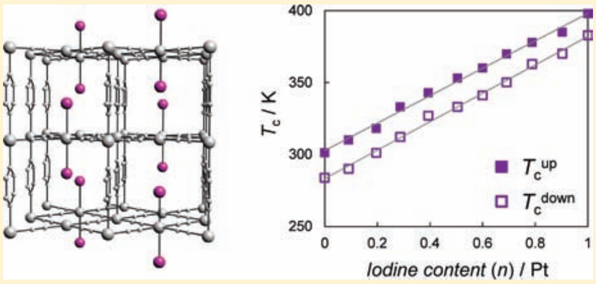
Supporting Information

ABSTRACT: Precise control of spin transition temperature (T_c) is one of the most important challenges in molecular magnetism. A Hofmann-type porous coordination polymer $\{Fe(pz)[Pt^{II}(CN)_4]\}$ (**1**; pz = pyrazine) exhibited cooperative spin transition near room temperature ($T_c^{up} = 304$ K and $T_c^{down} = 284$ K) and its iodine adduct $\{Fe(pz)[Pt^{II/IV}(CN)_4(I)]\}$ (**1-I**), prepared by oxidative addition of iodine to the open metal sites of Pt^{II}, raised the T_c by 100 K. DSC and microscopic Raman spectra of a solid mixture of **1-I** and **1** revealed that iodine migrated from **1-I** to **1** through the grain boundary after heating above 398 K. We have succeeded in precisely controlling the iodine content of $\{Fe(pz)[Pt(CN)_4(I)_n]\}$ (**1-I*n***; $n = 0.0-1.0$), which resulted in consecutive modulation of T_c in the range 300−400 K while maintaining the hysteresis width. Furthermore, it was demonstrated that iodine migration in the solid mixture was triggered by the spin transition of **1-I**. The magnetically bistable porous framework decorating guest interactive open-metal-site in the pore surface makes it possible to modulate T_c ad arbitrium through unique postsynthetic method using iodine migration.



■ INTRODUCTION

Spin transition (ST) is one of the most spectacular examples of molecule-based switchable materials based on $3d^4-3d^7$ coordination compounds, particularly well-known in iron(II) compounds ($3d^6$) whose electron configurations can move between the paramagnetic high-spin (HS) and the diamagnetic low-spin (LS) states with thermal hysteresis, and produce bistabilities in magnetic, optical, and structural properties.[1] Such ST compounds have been studied actively in relation to aspects of fundamental theory and applications such as sensors, displays, and switching devices. To implement ST compounds in such devices, it is essential to control the magnetic properties, that is, ST temperature (T_c) and hysteresis width, on demand. Until now, a chemical method that randomly intercalates different kinds of metal ions and a physical method using external pressure were used to control T_c.[2] These methods were useful for modulating T_c by tuning the ligand field, but on the other hand, often faced a problem that the ST hysteresis faded because of reduced cooperativity induced by fragmentation of the magnetic domain.[2a−f] Also ligand substitution and counterion size change were available for controlling T_c, which become particularly operative in the case of 1-D Fe(II)-triazole-type chain compounds.[2f,g] However, there are currently few reports of precise T_c adjustment without changing cooperativity. Here, we focus on porous compounds that exhibit ST and have regular and stable frameworks to deliver this aim. The regular porous framework allows guest molecules to disperse entirely and homogeneously, which promises to be useful for preventing reduction of the cooperativity and for modulating T_c via a postsynthetic method.

Received: January 10, 2011
Published: April 28, 2011

Porous materials provide attractive space for functions, for example, guest adsorption,[3] heterogeneous catalysis,[4] and proton conduction.[5] In particular, porous coordination polymers (PCPs) or metal−organic frameworks (MOFs) that have highly regular, designable, and flexible pores based on coordination bonds have attracted much attention as a new class of porous materials in the past decade. Such PCPs are expected to be multifunctional platforms combining porous properties with specific chemical and physical properties.[6] A few pioneering PCPs exhibiting spin crossover have already been prepared, but their T_c values were far from room temperature.[7] Recently, Hofmann-type PCPs {Fe(pz)[$M^{II}(CN)_4$]} (pz = pyrazine; M^{II} = Ni, Pd, Pt) have been reported as new chemoresponsive PCPs switching spin states through guest adsorption processes at room temperature.[2b,c,8] These PCPs form a three-dimensional pillared-layer-type porous framework consisting of cyano-bridged $Fe^{II}M^{II}$ bimetallic layers and interlayer pz-bridges, adsorb various guest molecules, and show ST with hysteresis of ca. 20 K near room temperature. The spin state of Fe^{II} sites were switched between HS and LS states depending on the guest molecules and host−guest interactions; for example, the HS state was stabilized by hydroxylic solvents and five- and six-membered aromatic molecules, while the LS state was stabilized by CS_2 (for M = Pt, Pd, Ni), I^- (for M = Pt), and CH_3CN (for M = Ni) at 298 K. Guest molecules are confined in the pores, interacting weakly with the pz pillar ligands or the M^{II} centers. In the particular case of iodine, the guest-free {Fe(pz)[$Pt^{II}(CN)_4$]} (**1**) undergoes an oxidative addition reaction involving rapid diffusion of iodine molecules into the pores of **1** followed by electron transfer from half of Pt^{II} ions to iodine molecules to give Pt−I bonds with concomitant cleavage of the molecular iodine bond. The axial positions of Pt in the resulting iodide adduct {Fe(pz)[$Pt^{II/IV}(CN)_4(I)$]} (**1-I**) are occupied by two iodide anions with half occupancy, namely, there are twice as many available positions as iodine atoms; consequently, the holes and iodine atoms are uniformly and randomly distributed in the crystal. It is well-known that the presence of large amounts of spare available positions facilitates atomic mobility from concentrated to diluted regions of the crystal. Compound **1-I** strongly stabilized the LS state and exhibited ST (T_c^{up} = 398 K and T_c^{down} = 383 K) with a hysteresis width similar to **1**. The porous framework of **1** demonstrated high stability toward oxidative addition of iodine with an increase in T_c by ca. 100 K and maintained the cooperativity of ST. From these results, we conceived the modulation of ST temperature T_c by controlling the chemically adsorbed iodine content. To precisely control the amount of iodine introduced, we developed a new postsynthetic method that directly blended the iodine adduct **1-I** and guest-free **1** in an arbitrary ratio. Here, we applied chemical migration between the regular and stable porous compounds, which successfully resulted in precise and consecutive control of the iodine content without byproducts and in modulation of T_c in the range of 300−400 K at will.

EXPERIMENTAL SECTION

Materials. Chemicals were purchased from commercial sources and used without further purification. Guest-free {M(pz)[$Pt(CN)_4$]} (M = Fe (**1**), Ni (**2**)) and Iodine adducts {M(pz)[$Pt^{II/IV}(CN)_4(I)$] } (M = Fe (**1-I**), Ni (**2-I**)) were prepared according to the literature method.[8a−d] Details are given in Supporting Information (Table S1).

Physical Measurements. Magnetic susceptibilities of all samples were measured by Quantum Design MPMS-XL5R SQUID in the temperature range 200−400 K (settle mode) in an applied dc field of 1000 Oe. X-ray powder diffraction (XRPD) was collected on a Rigaku RINT 2000 Ultima diffractometr with Cu−Kα radiation. Thermogravimetric analysis was performed at 10 K min^{-1} using a Rigaku Instrument Thermo plus TG 8120 in a nitrogen atmosphere. DSC analysis was carried out with a Seiko Instruments DSC 6220 under N_2 atmosphere. The weight of the samples ranged from 2 to 4 mg. The microscopic Raman spectroscopy was carried out by LabRAM HR-800 spectrometer (HORIBA Jobin Yvon Ltd.) at temperature in the range of 300−423 K using an LK-600 hot stage (Linkam). A 785-nm semiconductor laser was used for excitation source. The solid-state transmission spectra were measured by JASCO MSV-370 microUV−vis-NIR spectrometer with a Linkam THM600 hot stage with programmable temperature controllers L-600A and LK600PM under Ar atmosphere. Elemental Analysis of carbon, hydrogen, and nitrogen was carried out on a Flash EA 1112 series, Thermo Finnigan instrument.

RESULTS AND DISCUSSIONS

Control of Iodine Content. We have already reported that the four-coordinated Pt^{II} centers in {Fe(pz)[$Pt^{II}(CN)_4$]} (**1**) can perform as open-metal sites to interact strongly with π-donor molecules like iodine. Combined crystallographic and Pt4f-XPS data for the iodine adduct {Fe(pz)[$Pt^{II/IV}(CN)_4(I)$]} (**1-I**) revealed chemisorption of iodine molecules and suggested an alternate arrangement of $[Pt^{IV}(CN)_4(I)_2]^{2-}$ and coordinatively unsaturated $[Pt^{II}(CN)_4]^{2-}$ in the porous framework (Figure 1). Compared with the solid-state transmission spectra of **1** and **1-I** in both states, essentially similar spectra were observed in the HS state, on the other hand the adsorption band of **1-I** covered a larger visible region than that of **1** in the LS state (Figure S1). This difference in the LS state is attributed to the presence of the Pt^{IV}−I and the CT band from LS Fe^{II} to Pt^{IV}.[9] This band appears to be operative only in the LS Fe^{II} with fully occupied t_{2g} orbitals. Because Pt^{II} and Pt^{IV} were not bridged by iodine in the lattice, the mixed-valence CT bands from Pt^{II} to Pt^{IV} moieties were not observed in both spin states in the range of 300−2000 nm. The

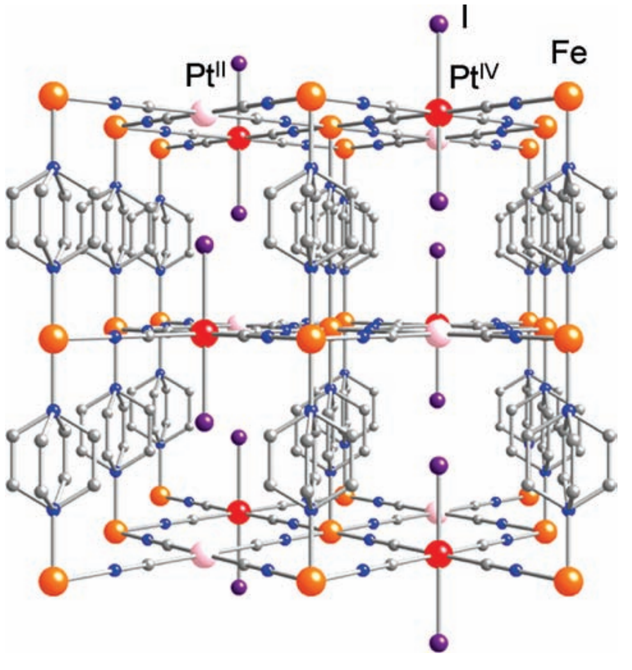


Figure 1. Crystal structure of {Fe(pz)[$Pt^{II/IV}(CN)_4(I)$]} (**1-I**). Atoms: Fe (orange), Pt^{II} (pink), Pt^{IV} (red), I (purple), C (gray), N (blue).

coordination of iodide anions resulted in T_c rising to 398 K with a hysteresis width of 15 K (Figure 2). The strong π-donor capability of iodide enhances the σ-donor capability of cyano nitrogen through Pt^{IV}, and increases ligand field strength around Fe^{II}. This result suggests that ST behavior can be controlled by guest molecules on the open metal site in the vicinity of Fe^{II} centers, and implies that T_c may be modulated by iodine content in this case. In general, it is difficult to control the vapor pressure and amount of iodine introduced. In fact, the method using iodine vapor did not work well. Here, we carried out a solid-state reaction method by blending and carefully grinding compounds **1-I** and **1** and heating the solid mixture (solid-state blending and heating (SBH) method) to control the iodine content precisely taking advantage of iodine mobility in **1-I**.

First, the solid mixture was prepared by blending **1-I** with **1** in a 1:1 molar ratio using an agate mortar. The DSC curve of the solid mixture showed that two different sets of peaks originated from each spin transition of **1-I** (ca. 397 K (endo)) and **1** (ca. 280 K (exo) and 297 K (endo)) during the first scan (Figure 3a). During the second successive scan, the former peaks disappeared completely and a single new set of peaks appeared at ca. 335 K (exo) and 350 K (endo), which suggested formation of a homogeneous phase after heating. The exo peak of **1-I** was not observed during the first scan because the iodine migration occurred after appearing the endo peak, that is, after ST of **1-I** (see the section of Iodine Migration). The TGA curve of the heat-treated mixture (heated at 423 K for 180 min) showed weight loss of ca. 28.8% around 500 K, which substantially corresponds to 0.5 iodine anions and one pz ligand per unit. The iodine content of the mixture was determined to be half of the **1-I** content (Figure 3b). These results indicated that the **1-I** iodine migrated to the guest-free **1** and diffused throughout the solid, and the blended material changed from heterogeneous solid **1-I** and **1** to a homogeneous solid formulated as $\{Fe(pz)[Pt^{II/IV}(CN)_4(I)_{0.5}]\}$ (**1-I$_{0.5}$**).

Control of Spin Transition Temperature T_c. By applying the SBH method, the iodine content of $\{Fe(pz)[Pt(CN)_4(I)_n]\}$ (**1-I*n***; n = 0.0−1.0) could be precisely and consecutively controlled just by changing the blend ratio between **1-I** and **1** from 0:10 to 10:0. All compounds showed the same X-ray powder diffraction (XRPD) pattern at room temperature (Figure S2). All **1-I*n*** samples showed a set of DSC anomalies attributed to the ST. For example, the magnetic behavior of **1-I$_{0.5}$** clearly showed ST at T_c of 353 and 333 K during the heating and cooling processes, respectively. The values of T_c were consistent with the temperatures of DSC anomalies. The value of $\chi_M T$ of **1-I*n*** in the LS state is slightly larger than that of **1**. The residual HS fraction would be attributed to generation of defects on the surface of microcrystals due to grinding/blending the samples and oxidative addition of I_2. The defects give different coordination environment to Fe^{II} centers from inside of them. All **1-I*n*** samples were homogeneous and exhibited ST with similar curve shapes and hysteresis widths

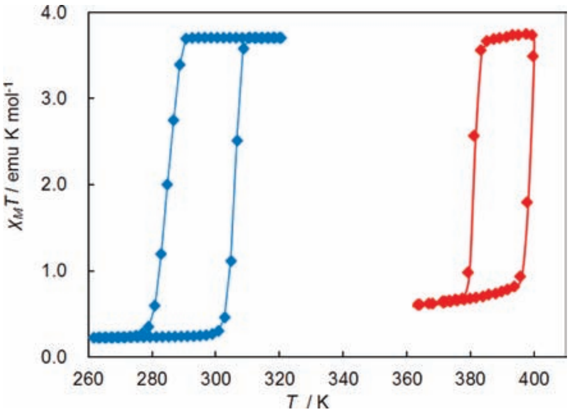


Figure 2. Magnetic behavior of **1** (blue) and **1-I** (red).

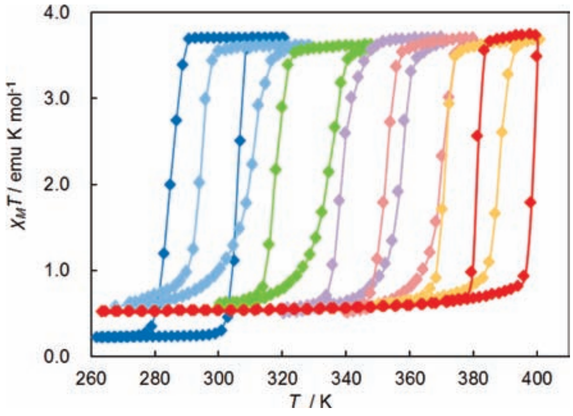


Figure 4. Magnetic behavior of $\{Fe(pz)[Pt(CN)_4(I)_n]\}$ (**1-I*n***); n = 0.0 (blue); 0.1 (sky blue); 0.3 (green); 0.5 (violet); 0.7 (pink); 0.9 (orange); 1.0 (red).

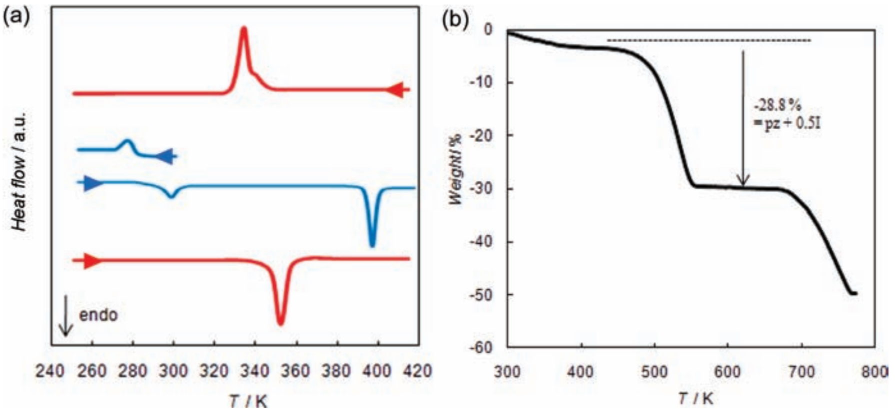


Figure 3. (a) DSC curves of the solid mixture of **1** and **1-I** (first scan blue and second scan red). (b) TGA curve of the solid mixture after heating at 423 K.

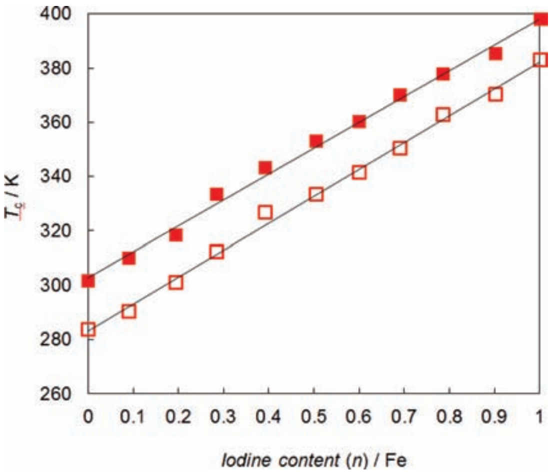


Figure 5. Correlation between T_c and the iodine content (n); T_c^{up} (■) and T_c^{down} (□).

(ca. 20 K) at unique temperatures (300−400 K) in response to the iodine content (Figure 4). It is noteworthy that the ST temperatures during heating (T_c^{up}) and cooling (T_c^{down}) correlated positively and linearly with iodine content (Figure 5). The respective correlations could be expressed using the following equations.

$$T_c^{up}:T = 96.4n + 302$$

$$T_c^{down}:T = 99.9n + 282$$

The iodine content dependence of the ST behavior of **1-I*n*** means that **1-I*n*** maintains the cooperativity of ST with homogeneous distribution of iodine throughout the solid and without fragmentation of the framework during application of the SBH method. Finally, the average ligand field strength around Fe^{II} in a certain domain size could be readily tuned chemically by modulating the iodine content. The regular and stable porous magnetic framework and interactive open metal sites play essential roles in forming the homogeneous solid through iodine migration. The process of iodine migration is discussed in the next section.

Iodine Migration. The iodine migration phenomenon was corroborated by DSC and variable-temperature microscopic Raman spectroscopy studies.

First, the DSC curve of the full iodine adduct **1-I** was checked repeatedly in the temperature range 303−423 K. The characteristic endo (at 395 K) and exo (at 378 K) peaks attributed to ST did not shift under the measurement conditions after several cycles (Figure S3a). When **1-I** was heated above 450 K, the iodine was removed with accompanying decomposition of the sample (Figure S3b). These results suggest that iodine is retained at the open metal site (Pt^{IV}) and not released below 423 K. To examine the iodine migration process, the full iodine adduct **1-I** and guest-free **1** were placed separately without physical contact in a DSC sample pan. The "noncontact" samples showed DSC anomalies characteristic to each compound in the range of 243−403 K, and the peak positions did not shift after several cycles (Figure S3). On the other hand, a solid mixture of **1-I** and **1** ("contact" sample) showed that both sets of initial DSC peaks faded and a new set of peaks appeared at the midpoint of the initial peaks in the second cycle, as shown in Figure 3a. These experiments demonstrated that iodine migrated from **1-I** to **1** before decomposition (below 423 K) only under the contact condition. Thus, iodine migrated through the grain boundary between **1-I** and **1**, not through the air.

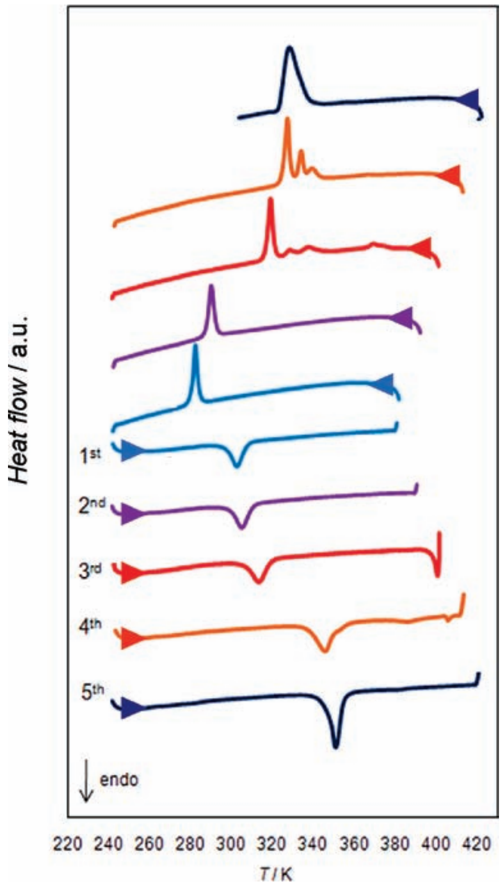


Figure 6. DSC curves of the solid mixture (**1-I**:**1** = 1:1), increasing the upper temperature limit by 10 K with every cycle (1st cycle blue; 2nd cycle purple; 3rd cycle red; 4th cycle orange; 5th cycle dark blue).

Next, temperature dependence of iodine migration was examined. DSC of the solid mixture (**1-I**:**1** = 1:1) was measured with increasing upper temperature limit by 10 K from 383 K in every cycle (Figure 6). The initial peaks of **1** did not shift below 393 K (2nd cycle). During the heating process of the third cycle, the endothermic anomaly of **1-I** appeared at 403 K, whereas the exothermic anomaly of **1-I** was not observed and the peak of **1** started shifting to higher temperature (ca. 320 K) suddenly in the successive cooling process (after heating to 403 K). Both peaks eventually merged into a single species peak in the following cycles, which suggested that iodine migration was triggered by the spin transition of **1-I** (T_c^{up} = 398 K).

For more direct demonstration of iodine migration, variable-temperature microscopic Raman spectroscopy was applied. The Raman shifts of **1-I** and **1** in the HS state were measured at 423 and 333 K, respectively (Figure 7). Compared with the Raman shift of **1**, most of the peaks of **1-I** were identical except for a very strong Pt−I vibration peak (129 cm^{-1}) that could be used as a probe signal for monitoring iodine migration. To observe the iodine migration, a composite disk with a plain interface between **1-I** (side **1-I**) and **1** (side **1**) was prepared (Figure S5). The Raman laser was focused on a point on the side **1** that is 90 μm far from the interface, and then the Raman shift was measured with the increase of temperature from 333 to 413 K. The Raman shift

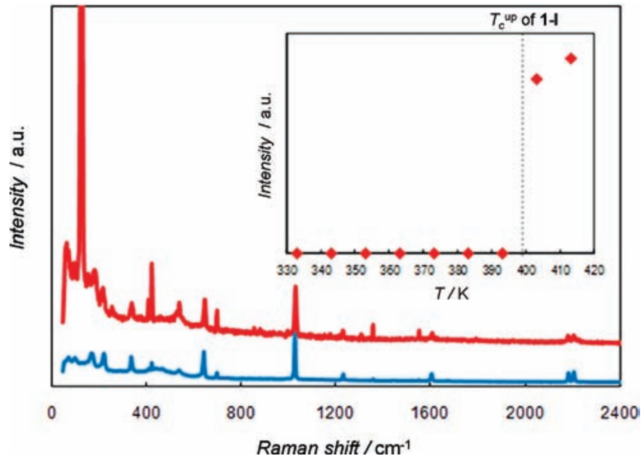


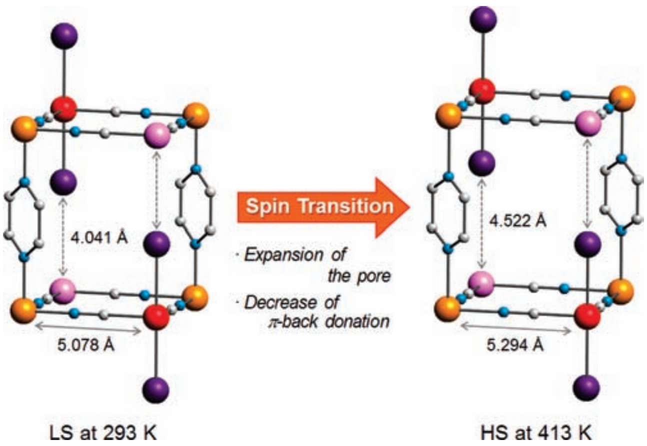
Figure 7. Raman spectra of **1** (HS) at 333 K (blue) and **1-I** (HS) at 423 K (red). Inset: Temperature dependence of the intensity ratio of Pt—I vibration on the **1** side, where the intensity ratio was estimated from the peaks for pyrazine vibration[8e] of 1028 cm^{-1} and Pt—I vibration of 129 cm^{-1}.

remained constant below 393 K. When the temperature reached 403 K, that is, when the ST of **1-I** occurred, the Pt—I vibration signal appeared abruptly on the side **1** (Figure 7 (inset)). The Pt—I peak was observed even at the far edge of the side **1** after heating. On the contrary, the intensity of the Pt—I peak on the side **1-I** immediately decreased above 403 K (Figure S6). These results clearly demonstrated that iodine migrated from **1-I** to **1** and the chemical migration is triggered by the ST of **1-I**. Moreover, the same measurement was carried out using another composite disk consisting of **1** and **1-I$_{0.5}$** (T_c^{up} = 353 K) to confirm the ST-induced iodine migration (Figure S7). Even in this case, iodine migrated from **1-I$_{0.5}$** to **1** above T_c^{up} of **1-I$_{0.5}$** in the same fashion. No vibration peak of iodine molecule, I_2, was observed around 200 cm^{-1} in both measurements, which indicated that the state of iodine was not I_2 during the migration.

The mechanism of ST-induced iodine migration can be discussed in terms of changes in the pore size and electronic contribution of Fe^{II}. For the LS state of **1-I**, iodide binds on open metal sites (axial positions of Pt^{IV}) with I—Pt^{IV} distance of 2.714(3) Å and I···Pt^{II} (opposite side) separation of 4.041(5) Å at 293 K in the pore. After the ST of **1-I**, the I···Pt^{II} separation was extended to 4.522(16) Å and the pore was expanded by 16.22%, which provides sufficient space to release and transfer iodine. In addition, π-back-donation from Fe^{II} to cyano bridges decreases in the HS state, which reduces the electron density of Pt^{IV}, changes its redox potential, and finally weakens the I—Pt^{IV} bond (Scheme 1).

To corroborate the ST-induced iodine migration, the HS compound $\{Ni(pz)[Pt(CN)_4]\}$ (**2**) and its iodine adduct $\{Ni(pz)[Pt(CN)_4(I)]\}$ (**2-I**) were prepared and the control experiments were carried out using the SBH method. The structures and electric states of **2** and **2-I** are close to those of **1** and **1-I** in the HS state. The DSC curve of a 1:1 solid mixture of **1** and **2-I** demonstrated that iodine partially migrated from **2-I** to **1** just by mixing without heating (Figure S7). Because **1** was changed to the LS state at room temperature (RT), meaning shrinkage of the pore, by adsorbing the small amount of iodine ($n < 0.1$), the iodine did not migrate entirely. After heating to 420 K, the solid mixture showed DSC anomalies attributed to the ST at 330 K (exo) and 348 K (endo). The ST temperature corresponds to that of **1-I$_{0.5}$**. On the other hand, the 1:1 solid mixture of **1-I** and **2** showed iodine migration only after heating over 400 K. These results highlighted the significance of structural and electronic contributions of the HS state for iodine migration.

Scheme 1. Proposed Mechanism of ST-Induced Iodine Migration[a]



[a] Atoms: Fe (orange), Pt^{II} (pink), Pt^{IV} (red), I (purple), C (gray), N (blue).

Iodine migration was well corroborated by DSC and microscopic Raman spectroscopy; however, it is still unclear what sort of iodine species are generated and moves through the pore. The migration of I^- should be accompanied by the redox reaction of Pt^{IV}; however, we could not give the clear evidence of this mechanism by dielectric or conductivity measurements. Further investigations of the migration mechanism are in progress using solid state iodine NMR and ^{129}I Mossbauer spectroscopy.

■ CONCLUSION

We have successfully controlled the iodine content of the porous magnetic compound $\{Fe(pz)[Pt(CN)_4(I)_n]\}$ (**1-I*n***) in the range of n = 0.0—1.0 using the SBH method, and consecutively modulated the T_c value of **1-I*n*** from 300 to 400 K while maintaining cooperativity. Heating a blend of the full iodine adduct **1-I** and guest-free **1** caused iodine migration to be initiated. The chemically adsorbed iodine migrated from **1-I** to **I** above 400 K, and the chemical migration resulted in the formation of a homogeneous solid. Moreover, the iodine migration was triggered by the ST of **1-I** associated with expanding pores and reducing the contribution of π-back-donation. Precise control and consecutive modulation of T_c were achieved using the SBH method with PCPs having regular, stable, and interactive pores, though the detailed mechanism of iodine migration remains unsolved. The simple and byproduct-free postsynthetic method will be applicable for modulating the various functions of coordination compounds ad arbitrium, and useful for developing functional space materials.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Synthetic methods, reflectance spectra, solid-state transmission spectra, XRPD patterns of **1-I*n***, DSC curves of **1-I** and the 'noncontact' samples of **1-I** and **1**, TGA curve of **1-I** and Raman spectra of composite disk. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENT

This work was supported by a Grant-In-Aid for Science Research in a Priority Area ‘Coordination Programming (No. 22108512)’, a Grant-In-Aid for Scientific Research Program (No. 23245014) and CREST/JST programme from the Ministry of Education, Culture, Sports, Science and Technology of Japan and the Spanish Ministerio de Ciencia e Innovación (MICINN) and FEDER funds (CTQ2010-18414). The authors thank Prof. Ho-Chol Chang for the measurements of solid state transmission spectra.

■ REFERENCES

(1) (a) Real, J. A.; Gaspar, A. B.; Muñoz, M. C. *Dalton Trans.* **2005**, 2062.(b) *Spin Crossover in Transition Metal Compounds*; Gütlich, P., Goodwin, H. A., Eds.; Topics in Current Chemistry, Vol. 233, Springer: New York, 2004 (c) Real, J. A.; Gaspar, A. B.; Niel, V.; Muñoz, M. C. *Coord. Chem. Rev.* **2003**, *236*, 121. (d) Hayami, S.; Kawajiri, R.; Juhász, G.; Kawahara, T.; Hashiguchi, K.; Sato, O.; Inoue, K.; Maeda, Y. *Bull. Chem. Soc. Jpn.* **2003**, *76*, 1207. (e) Gütlich, P.; Garcia, Y.; Woike, T. *Coord. Chem. Rev.* **2001**, *219*, 839. (f) Gütlich, P.; Garcia, Y.; Goodwin, H. A. *Chem. Soc. Rev.* **2000**, *29*, 419. (g) Kahn, O.; Martínez, C. J. *Science* **1998**, *279*, 44. (h) Gütlich, P.; Hauser, A.; Spiering, H. *Angew. Chem., Int. Ed.* **1994**, *33*, 2024.

(2) (a) Nishino, M.; Boukheddaden, K.; Konishi, Y.; Miyashita, S. *Phys. Rev. Lett.* **2007**, *98*, 247203. (b) Tayagaki, T.; Galet, A.; Molnár, G.; Muñoz, M. C.; Zwick, A.; Tanaka, K.; Real, J. A.; Bousseksou, A. *J. Phys. Chem. B* **2005**, *109*, 14859. (c) Molnár, G.; Niel, V.; Real, J. A.; Dubrovinsky, L.; Bousseksou, A.; McGarvey, J. J. *J. Phys. Chem. B* **2003**, *107*, 3149. (d) Garcia, Y.; Koningbruggen, P. J.; Lapouyade, R.; Fournés, L.; Rabardel, L.; Kahn, O.; Ksenofontov, V.; Levchenko, G.; Gütlich, P. *Chem. Mater.* **1998**, *10*, 2426. (e) Galet, A.; Gaspar, A. B.; Muñoz, M. C.; Levchenko, G.; Real, J. A. *Inorg. Chem.* **2006**, *45*, 9670. (f) Kröber, J.; Codjovi, E.; Kahn, O.; Grolière, F.; Jay, C. *J. Am. Chem. Soc.* **1993**, *115*, 9810. (g) Garcia, Y.; Koningbruggen, P. J.; Lapouyade, R.; Rabardel, L.; Kahn, O.; Wieczorek, M.; Bronisz, R.; Ciunik, Z.; Rudlf, M. F. *C. R. Acad. Sci, Ser. II c: Chim.* **1998**, 523.

(3) (a) Phan, A.; Doonan, C. J.; Uribe-Romo, F. J.; Knobler, C. B.; O'Keeffe, M.; Yaghi, O. M. *Acc. Chem. Res.* **2010**, *43*, 58. (b) Furukawa, H.; Ko, N.; Go, Y. B.; Aratani, N.; Choi, S. B.; Choi, E.; Yazaydin, A. O.; Snurr, R. Q.; O'Keeffe, M.; Kim, J.; Yaghi, O. M. *Science* **2010**, *329*, 424. (c) Férey, G. *Chem. Soc. Rev.* **2008**, *37*, 191. (d) Kitagawa, S.; Kitaura, R.; Noro, S.-i. *Angew. Chem., Int. Ed.* **2004**, *43*, 2334. (e) Yaghi, O. M.; O'Keeffe, M.; Ockwig, N. W.; Chae, H. K.; Eddaoudi, M.; Kim, J. *Nature* **2003**, *423*, 705.

(4) (a) Ma, L.; Abney, C.; Lin, W. *Chem. Soc. Rev.* **2009**, *38*, 1248. (b) Hasegawa, S.; Horike, S.; Matsuda, R.; Furukawa, S.; Mochizuki, K.; Kinoshita, Y.; Kitagawa, S. *J. Am. Chem. Soc.* **2007**, *129*, 2607. (c) Zou, R. Q.; Sakurai, H.; Xu, Q. *Angew. Chem., Int. Ed.* **2006**, *45*, 2542. (d) Seo, J. S.; Whang, D.; Lee, H.; Jun, S. I.; Oh, J.; Jeon, Y. J.; Kim, K. *Nature* **2000**, *404*, 982.

(5) (a) Bureekaew, S.; Horike, S.; Higuchi, M.; Mizuno, M.; Kawamura, T.; Tanaka, D.; Yanai, N.; Kitagawa, S. *Nat. Mater.* **2009**, *8*, 831. (b) Hurd, J. A.; Vaidhyanathan, R.; Thangadurai, V.; Ratcliffe, C. I.; Moudrakovski., I. L.; Shimizu, G. K. *Nat. Chem.* **2009**, *1*, 705. (c) Ōkawa, H.; Shigematsu, A.; Sadakiyo, M.; Miyagawa, T.; Yoneda, K.; Ohba, M.; Kitagawa, H. *J. Am. Chem. Soc.* **2009**, *131*, 13516. (d) Sadakiyo, M.; Yamada, T.; Kitagawa, H. *J. Am. Chem. Soc.* **2009**, *131*, 9906.

(6) (a) Shimomura, S.; Higuchi, M.; Matsuda, R.; Yoneda, K.; Hijikata, Y.; Kubota, Y.; Mita, Y.; Kim, J.; Takata, M.; Kitagawa, S. *Nat. Chem.* **2010**, *2*, 633. (b) Kobayashi, Y.; Jacobs, B.; Allendorf, M. D.; Long, J. R. *Chem. Mater.* **2010**, *22*, 4120. (c) Long, J. R.; Yaghi, O. M. *Chem. Soc. Rev.* **2009**, *38*, 1213. (d) Horike, S.; Shimomura, S.; Kitagawa, S. *Nat. Chem.* **2009**, *1*, 695. (e) Li, J.-R.; Kuppler, R. J.; Zhou, H. C. *Chem. Soc. Rev.* **2009**, *38*, 1477. (f) Guo, Z.; Cao, R.; Wang, X.; Li, H.; Yuan, W.; Wang, G.; Wu, H.; Li, J. *J. Am. Chem. Soc.* **2009**, *131*, 6894. (g) Jain, P.; Ramachandran, V.; Clark, R. J.; Zhou, H. D.; Toby, B. H.; Dalal, N. S.; Kroto, H. W.; Cheetham, A. K. *J. Am. Chem. Soc.* **2009**, *131*, 13625. (h) Takaishi, S.; Hosoda, M.; Kajiwara, T.; Miyasaka, H.; Yamashita, M.; Nakanishi, Y.; Kitagawa, Y.; Yamaguchi, K.; Kobayashi, A.; Kitagawa, H. *Inorg. Chem.* **2009**, *48*, 9048. (i) Kaneko, W.; Ohba, M.; Kitagawa, S. *J. Am. Chem. Soc.* **2007**, *129*, 13706. (j) Yanai, N.; Kaneko, W.; Yoneda, K.; Ohba, M.; Kitagawa, S. *J. Am. Chem. Soc.* **2007**, *129*, 3496. (k) Ohkoshi, S.; Tsunobuchi, Y.; Takahashi, H.; Hozumi, T.; Shiro, M.; Hashimoto, K. *J. Am. Chem. Soc.* **2007**, *129*, 3084. (l) Maspoch, D.; Molina, S. R.; Veciana, J. *Chem. Soc. Rev.* **2007**, *36*, 770. (m) Kepert, C. J. *Chem. Commun.* **2006**, 696. (n) Kurmoo, M.; Kumagai, H.; Chapman, K. W.; Kepert, C. J. *Chem. Commun.* **2005**, 3012. (o) Cui, H. B.; Takahashi, K.; Okano, Y.; Kobayashi, H.; Wang, Z.; Kobayashi, A. *Angew. Chem., Int. Ed.* **2005**, *44*, 6508. (p) Ohkoshi, S.; Arai, K.; Sato, Y.; Hashimoto, K. *Nat. Mater.* **2004**, *3*, 857. (q) Wang, Z.; Zhang, B.; Fujiwara, H.; Kobayashi, H.; Kurmoo, M. *Chem. Commun.* **2004**, 416. (r) Maspoch, D.; Molina, D. R.; Wurst, K.; Domingo, N.; Cavallini, M.; Biscarini, F.; Tejada, J.; Rovira, C.; Veciana, J. *Nat. Mater.* **2003**, *2*, 190.

(7) (a) Halder, G. J.; Chapman, K. W.; Neville, S. M.; Moubaraki, B.; Murray, K. S.; Létard, J. F.; Kepert, C. J. *J. Am. Chem. Soc.* **2008**, *130*, 17552. (b) Neville, S. M.; Halder, G. J.; Chapman, K. W.; Duriska, M. B.; Southon, P. D.; Cashion, J. D.; Letard, J. F.; Moubaraki, B.; Murray, K. S.; Kepert, C. J. *J. Am. Chem. Soc.* **2008**, *130*, 2869. (c) Niel, V.; Thompson, A. J.; Muñoz, M. C.; Galet, A.; Goeta, A. E.; Real, J. A. *Angew. Chem., Int. Ed.* **2003**, *42*, 3760. (d) Halder, G. J.; Kepert, C. J.; Moubaraki, B.; Murray, K. S.; Cashion, J. D. *Science* **2002**, *298*, 1762. (e) Real, J. A.; Andrés, E.; Muñoz, M. C.; Julve, M.; Granier, T.; Bousseksou, A.; Varret, F. *Science* **1995**, *268*, 265.

(8) (a) Niel, V.; Martínez-Agudo, J. M.; Muñoz, M. C.; Gaspar, A. B.; Real, J. A. *Inorg. Chem.* **2001**, *40*, 3838. (b) Ohba, M.; Yoneda, K.; Agustí, G.; Muñoz, M. C.; Gaspar, A. B.; Real, J. A.; Yamasaki, M.; Ando, H.; Nakao, Y.; Sakaki, S.; Kitagawa, S. *Angew. Chem., Int. Ed.* **2009**, *48*, 4767. (c) Agustí, G.; Ohtani, R.; Yoneda, K.; Gaspar, A. B.; Ohba, M.; Sánchez-Royo, J. F.; Muñoz, M. C.; Kitagawa, S.; Real, J. A. *Angew. Chem., Int. Ed.* **2009**, *48*, 8944. (d) Southon, P. D.; Liu, L.; Fellows, E. A.; Price, D. J.; Halder, G. J.; Chapman, K. W.; Moubaraki, B.; Murray, K. S.; Létard, J. F.; Kepert, C. J. *J. Am. Chem. Soc.* **2009**, *131*, 10998. (e) Cobo, S.; Ostrovskii, D.; Bonhommeau, S.; Vendier, L.; Molnár, G.; Salmon, L.; Tanaka, K.; Bousseksou, A. *J. Am. Chem. Soc.* **2008**, *130*, 9019. (f) Boldog, I.; Gaspar, A. B.; Martínez, V.; Pardo-Ibáñez, P.; Ksenofontov, V.; Bhattacharjee, A.; Gütlich, P.; Real, J. A. *Angew. Chem., Int. Ed.* **2008**, *47*, 6433. (g) Volatron, F.; Catala, L.; Riviére, E.; Gloter, A.; Stéphan, O.; Mallah, T. *Inorg. Chem.* **2008**, *47*, 6584. (h) Molnár, G.; Cobo, S.; Real, J. A.; Carcenac, F.; Daran, E.; Vieu, C.; Bousseksou, A. *Adv. Mater.* **2007**, *19*, 2163. (i) Bonhommeau, S.; Molnár, G.; Galet, A.; Zwick, A.; Real, J. A.; McGarvey, J. J.; Bousseksou, A. *Angew. Chem., Int. Ed.* **2005**, *44*, 4069.

(9) (a) Zhou, M.; Pfennig, B. W.; Steiger, J.; Engen, D. V.; Bocarsly, A. B. *Inorg. Chem.* **1990**, *29*, 24566. (b) Pfennig, B. W.; Bocarsly, A. B. *J. Phys. Chem.* **1992**, *96*, 226.