

Porous Materials

Engineering Homochiral Metal–Organic Frameworks by Spatially Separating 1D Chiral Metal–Peptide Ladders: Tuning the Pore Size for Enantioselective Adsorption

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Abstract: The reaction of the chiral dipeptide glycyl-L(S)-glutamate with Co^{II} ions produces chiral ladders that can be used as rigid 1D building units. Spatial separation of these building units with linkers of different lengths allows the engineering of homochiral porous MOFs with enhanced pore sizes, pore volumes, and surface areas. This strategy enables the synthesis of a family of isoreticular MOFs, in which the pore size dictates the enantioselective adsorption of chiral molecules (in terms of their size and enantiomeric excess).

The field of metal-organic frameworks (MOFs) have witnessed a rapid expansion over the last two decades, which is mainly because of their pore tunability, which allows the storage, separation, and conversion of desired molecules to be optimized.^[1] Pore characteristics (size, shape, chirality, and chemical environment) are essential for such functions, as they dictate which molecules can enter the pores as well as the affinity of the molecules that are adsorbed within the pores.^[2] One of the most effective ways to control the pore size in MOFs is by rational connection of pre-designed, rigid building units (0D clusters, 1D chains, or 2D layers) through organic linkers.^[3] This approach, known as reticular synthesis, judiciously uses increasingly long linkers to expand pre-existing MOF structures by separating their characteristic building units.^[4] It can thus provide a series of isoreticular MOFs with larger pores. For instance, pores as large as 98 Å have been obtained for a series of MOFs isostructural to MOF-74 (or CPO-27) constructed by connecting their characteristic 1D Mg^{II} oxide unit through sequentially longer organic linkers: from dihydroxy-terephthalate up to eleven phenyl rings.^[5] Although several isoreticular MOF families have been reported, this approach has rarely been used to tune the pore size of homochiral MOFs.^[6] Reticular synthesis has been employed to generate a family of homochiral MOFs in which layers built up from Ni^{II} ions and L-aspartic acid are linked by pillar N-donor ligands such as 4,4'-bipyridine

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(bipy) and longer analogues of it.^[6a] In this case, although the pore size was increased, the pores were not accessible, as the use of ligands longer than bipy resulted in their crystallization within the pores, blocking these pores for sorption applications.^[6b] This approach has also been used by Dybtsev et al. to generate a second family of isoreticular homochiral MOFs in which the design of enhanced pore sizes enabled enantiose-lective adsorption of bulkier molecules that could not be adsorbed by the isoreticular MOFs with smaller pores.^[6c, d]

Among the chiral ligands available,^[7] naturally occurring peptides are an attractive family of chiral ligands that can be used for the synthesis of homochiral MOFs. They can be prepared using unlimited combinations of amino acids, and therefore they possess rich structural versatility and abundant coordination sites for metal binding. Although there are many peptides available, truly porous and robust peptide-based MOFs are still scarce. In fact, most of these MOFs show dynamic or compact structures since peptides are flexible and tend to fold owing to their aliphatic nature.^[8] These structural characteristics prevent their use for the separation of chiral molecules, which is of great importance, particularly in the pharmaceutical industry.^[7,9]

Herein, we report the use of a chiral peptide, glycyl-*L*(*S*)-glutamate (L-GG; Figure 1 a), to construct a chiral and rigid laddertype building unit (Co-L-GG) that we subsequently used in reticular synthesis. Specifically, we separated the unit spatially from its original non-porous assembly to obtain a series of isoreticular homochiral porous MOFs by using the bipy linker and extended versions of it. The resulting MOFs are based on noninterpenetrated networks, are robust upon guest removal and up to 320 °C, and are permanently porous to CO₂ (pore volumes: 0.118 cm³g⁻¹ to 0.256 cm³g⁻¹). We further show that the pore size in this family of homochiral MOFs dictates not only the size of the molecules that can be enantioselectively adsorbed, but also the adsorption efficiency, in terms of enantiomeric excess (*ee*).

We produced the one-dimensional Co-L-GG ladder-building unit by reacting $Co(OAc)_2$, H_2O and L-GG in a mixture of H_2O and MeOH (1:1) for 2 h at 80 °C (Figure 1 b, c). The infinite ladder units are constructed from the connection of octahedral Co^{II} centers through L-GG linkers. Each L-GG coordinates to three Co^{II} centers, whereas each Co^{II} center is bound to four O atoms (three from the carboxylate groups, and one from the carbonyl group) and one N atom (from the terminal amino group) of three consecutive L-GG linkers, and to one H₂O molecule, which points towards the neighboring 1D chains along the *c*-axis. In this configuration, the Co^{\parallel} ions are positioned at the vertices of the Co-L-GG ladders (Figure 1c). These ladders are stacked along the a-axis, and are strongly connected through several H-bonds (distances: 1.9 Å to 2.7 Å) involving the carboxylate and amino groups of the L-GG linkers of the neighboring ladders (Figure 1 d, e; Supporting Information, Figure S2). The ladders are also H-bonded along the *c*-axis, where the coordinated H_2O molecule is H-bonded (distance = 2.0 Å) to a carboxylate group of the L-GG linker of an adjacent ladder (Supporting Information, Figure S1). This arrangement yields a compact structure that lacks void volumes and is stable up





Figure 1. a) Representation of the dipeptide L(S)-GG. b) Illustration of the Co-L-GG ladders, highlighting the H₂O molecules (balls). c) A single ladder-type Co-L-GG building unit (represented with pink sticks). d) Representation of the H-bonding interactions occurred within three stacked Co-L-GG ladders along the *a*-axis. O red, N blue, H pale yellow, C gray, chiral C green, Co purple.^[16] e) Representation of the repetitive supramolecular 2D stacked Co-L-GG units. H-bonds are shown as curved lines. f) Illustration of the strategy used to spatially separate the Co-L-GG building units using bipy-type linkers of different lengths. Left: view along the *a*-axis; right: view along the *b*-axis.

to 400 $^\circ\text{C},$ as confirmed by thermogravimetric analysis (TGA; Supporting Information, Figure S4).

Our strategy for accessing the aforementioned non-porous homochiral structure entails replacing the coordinated terminal H₂O molecules of the Co-L-GG units with 4,4'-bipyridine (bipy)type linkers. Considering that the Co-L-GG units and their stacking are not affected by this process, these linkers are ideal for interlinking and spatially separating the 1D Co-L-GG units (and by extension, the entire 2D supramolecular stacked Co-L-GG layer) by a distance defined by the length of the linker used (Figure 1 f). Here, two neighboring units are connected through the vertices of the ladders. The resulting homochiral frameworks ensure incorporation of channels, the dimensions of which are defined by the shortest distance between two linkers bound to two neighboring vertices, and by the length of the linker. Moreover, the compactness of the 2D stacked Co-L-GG units prevents interpenetration, as there is not enough space for a bipy-type linker to penetrate them.

Following the above strategy, we reproduced the same synthesis to obtain Co-L-GG, except that we introduced the bipy linker. Interestingly, single-crystal X-ray diffraction (XRD) performed on crystals collected from the mother liquor revealed formation of $[Co-L-GG(bipy)_{0.5}]$ ·H₂O, Co-L-GGbipy_1, in which the 2D stacked chiral Co-L-GG units (identical to those described in the Co-L-GG structure; Figure 1d, e) were indeed interlinked by bipy linkers (Figure 2a, b). Thus, the framework exhibited channels with dimensions of 3.5×5.2 Å (considering vdW radii), which were filled with guest H₂O molecules. Importantly, a fraction of Co-L-GGbipy_1 showed structural changes

when it was exposed to the air. These changes involved a rotational disorder of the two pyridine rings of the bipy linker (Supporting Information, Figures S6, 7). This disorder results in the loss of symmetry, leading to formation of Co-L-GGbipy_2, which crystallizes in the triclinic *P*1 space group instead of the monoclinic *C*2 space group of Co-L-GGbipy_1. Co-L-GGbipy_2 showed the same framework topology, with slightly larger channels (3.6×5.7 Å, owing to the torsion of the two pyridine rings of the bipy linker; Figure 2 c), a total accessible volume per unit cell of 15% (corresponding to 115 Å³),^[10] and a pore volume of 0.094 cm³g⁻¹. Thus, when exposed to the air, a mixture of Co-L-GGbipy_1 and Co-L-GGbipy_2 coexisted. However, full conversion into Co-L-GGbipy_2 was observed when this mixture was fully desolvated, as confirmed by powder X-ray diffraction (PXRD; Supporting Information, Figures S9–S11).

Seeking to expand the Co-L-GGbipy framework, we repeated the above synthesis, except that instead of bipy, we used longer analogues of it, including 4,4'-azobipyridine (azobipy), 4,4'-azinebipyridine (azinebipy), and 1,4-bis(4-pyridylethenyl)benzene (bpeb). Single-crystal XRD revealed that both Co-L-GGazobipy and Co-L-GGazinebipy are isoreticular frameworks with expanded pore apertures of dimensions of 3.3×6.2 Å and 3.2×6.9 Å (considering vdW radii), respectively (Figure 2 d, e), which is in agreement with the fact that azobipy and azinebipy are longer than bipy. The total accessible volume per unit cell of Co-L-GGazobipy is 25% (227 Å³; pore volume: 0.126 cm³g⁻¹), and of Co-L-GGazinebipy, 18% (157 Å³; pore volume: 0.120 cm³g⁻¹). Here, the inconsistency observed between the void volumes and the length of the two pillar li-

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Figure 2. a) Stick representation of Co-L-GGbipy_2 showing the Co-L-GG ladder units linked by the bipy ligand. b) Representation of the H-bonding interactions occurred within two stacked 1D chains along *a*-axis, forming the same supramolecular 2D stacked unit shown in Figure 1 d, e. c)–e) Crystal structures of isoreticular Co-L-GGbipy_2, Co-L-GGazobipy, and Co-L-GGazine-bipy, showing enhanced pore sizes. f) Expected connectivity in Co-L-GGbpeb. O red, N blue, H pale yellow, C gray, chiral C green, Co purple.^[16] g) CO₂ isotherms collected at 195 K and 0.8 bar.

gands can be explained by the orientation of azobipy and azinebipy linkers in the structures. In Co-L-GGazinebipy, both pyridine rings of the azinebipy linkers point inside the channels and therefore, generate a smaller accessible pore volume than do the azobipy linkers in Co-L-GGazobipy.

We then explored even longer bpeb linkers, ultimately isolating intergrown flake-type crystals of Co-L-GGbpeb (Figure 2 f). Our efforts to grow larger crystals were not successful (Supporting Information, Figure S15), nor were our attempts to characterize the resulting crystals with synchrotron-radiation single-crystal XRD. Indexing the PXRD data of Co-L-GGbpeb with the software Topas 4.2 (Bruker AXS) yielded the following cell parameters: triclinic P1, a = 11.766(16) Å, b = 9.809(56) Å, c = 24.678(15) Å and $\alpha = 106.539(92)^{\circ}$, $\beta = 100.03(10)^{\circ}$ and $\gamma =$ 81.94(19)°, which were refined through a Le Bail fitting procedure with excellent agreement indicators (Rwp = 3.36%, Rp =2.66%, Rexp=0.52%; Supporting Information, Figure S16). These unit cell parameters are consistent with those derived from the single-crystal XRD of Co-L-GGbipy_2, Co-L-GGazobipy, and Co-L-GGazinebipy, confirming the formation of an isoreticular framework in which the c-axis is expanded to 24.679(15) Å. The only difference here is that the a-axis in Co-L-GGbpeb is twice as larger, which we reasoned was due to the asymmetry of two neighboring bpeb ligands running along this axis. Further evidence of the formation of the expanded isoreticular framework was also provided by elemental analysis, FTIR spectroscopy, and TGA. Elemental microanalysis suggested that the formula corresponds to the formation of a structure analogous to that of Co-L-GGbipy_2, but which contains bpeb rather than bipy. The FTIR spectrum of Co-L-GGbpeb revealed an almost identical fingerprint to that of the first three structures, with the characteristic C=O bands observed at comparable wavenumbers: Co-L-GG (1698/ 1677 cm⁻¹), Co-L-GGbipy_2 (1659/1650 cm⁻¹), Co-L-GGazobipy (1662/1649 cm⁻¹), Co-L-GGazinebipy (1661/1649 cm⁻¹), and Co-L-GGbpeb (1660/1647 cm⁻¹) (Supporting Information, Figure S17). Also, TGA revealed that Co-L-GGbpeb is stable up to 320 °C; a fact consistent with the high thermal stability of Co-L-GGbipy_2, Co-L-GGazobipy, and Co-L-GGazinebipy (Supporting Information, Figures S18, S20).

To evaluate the porosity of all of the isoreticular frameworks, we performed N₂ and CO₂ gas sorption measurements at 77 K and 195 K, respectively. Prior to these measurements, all of the frameworks were activated at 40 °C overnight under vacuum, and the activated samples were characterized by TGA and PXRD (Supporting Information, Figures S19, S20). In all cases, TGA indicated a very small weight loss (<1%), which most likely arises from adventitious contamination by atmospheric water incurred during analysis, confirming that all of the MOF pores were free of guest water molecules. Also, the simulated (derived from the single-crystal structures) and experimental (resulting from the activated samples) PXRD patterns were consistent, confirming their high structural integrity upon guest removal. N₂ isotherms on all four MOFs showed type II behavior characteristic of non-porous materials. In contrast, the CO₂ adsorption isotherms of the four activated frameworks revealed that all of them are porous (Figure 2g). This specific behavior (porous to CO₂ and non-porous to N₂) is not unusual in MOFs. We reasoned that this selectivity could be due to the existence of structural defects, structural changes during gas adsorption, and/or the pore surface functionalization attracting and activating only quadrupolar molecules such as CO₂.^[11]

The CO₂ adsorption showed a steep, stepwise uptake in the low-pressure region (0 < P < 0.06). In particular, the stepped CO₂ adsorption isotherms indicated that the frameworks are somewhat structurally flexible (for example, phase transition and/or movements of the pillar ligands), which is consistent with structural observations of Co-L-GGbipy_1 and Co-L-GGbipy_2.^[8c, 12] Above 0.06 bar, the CO₂ uptake of Co-L-GGbipy_2, Co-L-GGazobipy, and Co-L-GGazinebipy reaches saturation, whereas upon increasing the pressure in Co-L-GGbpeb, it increases. The following Brunauer-Emmett-Teller (BET) surface areas were calculated from the CO₂ sorption data $(0.05 < p/p^0 < 0.3)$: 261 m²g⁻¹ (Co-L-GGbipy_2), 299 m²g⁻¹ (Co-L-GGazobipy), 315 m^2g^{-1} (Co-L-GGazinebipy), and 601 m^2g^{-1} (Co-L-GGbpeb). The observed pore volumes were: 0.118 cm³g⁻¹ (Co-L-GGbipy_2), 0.146 cm³g⁻¹ (Co-L-GGazobipy), 0.166 cm³g⁻¹ (Co-L-GGazinebipy), and 0.256 cm³g⁻¹ (Co-L-GGbpeb). The pore volumes calculated from the CO₂ adsorption data are slightly greater than those calculated from the static structures, confirming that adsorption of CO₂ induces structural rearrangements (for example, rotation of the pyridine rings of the pillar ligands).

Chiral MOFs with high surface areas and multiple active pore sites are highly desired for the resolution of racemic molecules of interest and enantioselective catalysis.^[13] Herein, we have observed that the separation of the 2D stacked Co-L-GG units is reflected in the pore apertures, pore volumes, and BET surface areas, all of which increase with increasing linker length. This tunability allows one to study how enantiomeric adsorption and separation are affected by pore aperture, by comparing MOFs that are structurally equivalent except for in terms of this parameter.^[14] Our preliminary results in this area have shown that all of the synthesized MOFs can enantioselectively adsorb a small molecule such as glycidol (volume: 110 Å³), whereas only Co-L-GGbpeb, with its larger pore apertures, can enantioselectively adsorb a bulkier molecule such as hydrobenzoin (volume: 299 Å³). Both molecules were enantioselective adsorbed in favor of the S form. These results have also shown that while the total amount of adsorbed glycidol tends to increase (from Co-L-GGbipy_2 to Co-L-GGazobipy and to Co-L-GGazinebipy) with increasing pore size and pore volume, the ee tends to decrease. In the case of Co-L-GGbpeb, the ee is in comparable levels with that of Co-L-GGazinebipy.

In the above experiments, we immersed each activated isoreticular MOF in a solution containing a racemic mixture of either glycidol or hydrobenzoin at room temperature. After 48 h, the crystals were filtered and washed with diethyl ether to remove any traces of surface-bound molecules. All dried samples were immersed in anhydrous methanol and finally were heated at 40 °C for 4 h. This method allows for total extraction of adsorbed glycidol and hydrobenzoin without any harm to the MOFs, thereby enabling their re-use (see below). The ee values of glycidol and of hydrobenzoin in the extraction medium were measured using gas chromatography and highperformance liquid chromatography, respectively. The detected amounts of adsorbed glycidol were 1.13 $\rm mol_{glycidol}/\rm mol_{MOF}$ in Co-L-GGbipy_2, 1.31 mol_{alvcidol}/mol_{MOF} in Co-L-GGazobipy, 1.36 $mol_{alvcidol}/mol_{MOF}$ in Co-L-GGazinebipy, and 3.11 $mol_{glycidol}/mol_{MOF}$ in Co-L-GGbpeb. Inversely, the enantioselective adsorptions (Sglycidol over *R*-glycidol) were $54.1 \pm 1.0\%$ for Co-L-GGbipy_2, $38.2\pm2.0\%$ for Co-L-GGazobipy, $34.0\pm1.5\%$ for Co-L-GGazinebipy, and $37.8 \pm 1.0\%$ for Co-L-GGbpeb. As previously mentioned, hydrobenzoin was adsorbed only by Co-L-GGbpeb, in the amount of 1.28 mol_{hvdrobenzoin}/mol_{MOF} and with an ee (S-hydrobenzoin over *R*-hydrobenzoin) of $24.1 \pm 2.0\%$ (Supporting Information, Table S3).

The aforementioned results confirmed that we could create isoreticular homochiral MOFs with controlled porosity and employ them to selectively tune enantioselective adsorption of chiral molecules. We would like to highlight two of our principal findings with this strategy. First, by simply increasing the pore aperture in a given MOF, one can enantioselectively adsorb (and therefore, separate) chiral molecules of increasing size, as we observed with Co-L-GGbpeb and *S*-hydrobenzoin. Second, we observed an inverse correlation between the total amount of adsorbed glycidol and the enantioselective adsorption of the *S*-form: amongst the MOFs tested, Co-L-GGbipy_2

adsorbed the smallest amount of glycidol but exhibited the highest *ee*. We have posited that the smaller pore apertures of Co-L-GGbipy_2 might promote higher affinity (that is, stronger interactions) between the glycidol and the chiral pore-wall surfaces.^[15]

To provide evidence that the adsorbed S-enantioenriched glycidol or hydrobenzoin in these MOFs could be released without damaging them, we repeated the same glycidol adsorption process twice using a sample of Co-L-GGbipy_2 that we had pre-loaded once with glycidol and evacuated by immersion in methanol at 40 °C. In these second and third processes, the total amounts of adsorbed glycidol were 1.09 and 1.04 mol_{alvcidol}/mol_{MOF} and the *ee* (S-glycidol over *R*-glycidol) was 54.4 \pm 1.0 % and 55.0 \pm 1.5 %. The same process was repeated with the adsorption of hydrobenzoin in a sample of Co-L-GGbpeb, in which 3.01 and 3.08 mol_{glycidol}/mol_{MOF} were adsorbed in the second and third cycle, with an ee (S-hydrobenzoin over R-hydrobenzoin) of $28.8\pm4.0\%$ and $25.6\pm0.5\%$ (Supporting Information, Table S1). These results are comparable to those of the previous experiments, confirming that this isoreticular family of MOFs is sufficiently stable to be re-used for enantioselective adsorption, and that the adsorbed S-enantioenriched molecules can be fully released in methanol at 40°C, paving the way for their application in enantioseparation.

In conclusion, we have designed a family of isoreticular homochiral peptide-based MOFs through the linker extension strategy. These MOFs can be synthesized in high yields, and they exhibit high thermal stabilities and permanent porosity, which can be tuned through judicious choice of the type and size of linker. The MOFs were further tested for the enantioselective adsorption of chiral molecules and confirmed that their separation is size-dependent. This strategy has enabled us to better understand the formation and design peptide-based MOFs for chiral separation applications.^[7,9] Future studies will focus on extending the porosity of this isoreticular family of MOFs for the adsorption and separation of large drug molecules in which the *R*- and *S*-enantiomers have different effects.

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- a) M. D. Allendorf, V. Stavila, *Cryst. Eng. Comm.* 2015, *17*, 219; b) H. Furukawa, K. E. Cordova, M. OKeeffe, O. M. Yaghi, *Science* 2013, *341*, 1230444; c) T. A. Makal, J.-R. Li, W. Lu, H.-C. Zhou, *Chem. Soc. Rev.* 2012, *41*, 7761; d) Y. He, W. Zhou, G. Qian, B. Chen, *Chem. Soc. Rev.* 2014, *43*, 5657.
- [2] a) M. Majumder, P. Sheath, J. I. Mardel, T. G. Harvey, A. W. Thornton, A. Gonzago, D. F. Kennedy, I. Madsen, J. W. Taylor, D. R. Turner, M. R. Hill, *Chem. Mater.* 2012, *24*, 4647; b) W. L. Queen, M. R. Hudson, E. D. Bloch, J. A. Mason, M. I. Gonzalez, J. S. Lee, D. Gygi, J. D. Howe, K. Lee, T. A. Darwish, M. James, V. K. Peterson, S. J. Teat, B. Smit, J. B. Neaton, J. R. Long, C. M. Brown, *Chem. Sci.* 2014, *5*, 4569; c) M. T. Kapelewski, S. J. Geier, M. R. Hudson, D. Stuck, J. A. Mason, J. N. Nelson, D. J. Xiao, Z. Hulvey, E. Gilmour, S. A. FitzGerald, M. Head-Gordon, C. M. Brown, J. R. Long, *J. Am. Chem. Soc.* 2014, *136*, 12119.
- [3] a) N. L. Rosi, J. Kim, M. Eddaoudi, B. L. Chen, M. OKeeffe, O. M. Yaghi, J. Am. Chem. Soc. 2005, 127, 1504; b) L. Liu, K. Konstas, M. R. Hill, S. G. Telfer, J. Am. Chem. Soc. 2013, 135, 17731.
- [4] O. M. Yaghi, M. OKeeffe, N. W. Ockwig, H. K. Chae, M. Eddaoudi, J. Kim, *Nature* 2003, 423, 705.
- [5] H. X. Deng, S. Grunder, K. E. Cordova, C. Valente, H. Furukawa, M. Hmadeh, F. Gandara, A. C. Whalley, Z. Liu, S. Asahina, H. Kazumori, M. OKeeffe, O. Terasaki, J. F. Stoddart, O. M. Yaghi, *Science* **2012**, *336*, 1018.
- [6] a) R. Vaidhyanathan, D. Bradshaw, J. N. Rebilly, J. P. Barrio, J. A. Gould, N. G. Berry, M. J. Rosseinsky, Angew. Chem. Int. Ed. 2006, 45, 6495; Angew. Chem. 2006, 118, 6645; b) J. Pérez-Barrio, J. N. Rebilly, B. Carter, D. Bradshaw, J. Bacsa, A. Y. Ganin, H. Park, A. Trewin, R. Vaidhyanathan, A. I. Cooper, J. E. Warren, M. J. Rosseinsky, Chem. Eur. J. 2008, 14, 4521; c) D. N. Dybtsev, A. L. Nuzhdin, H. Chun, K. P. Bryliakov, E. P. Talsi, V. P. Fedin, K. Kim, Angew. Chem. Int. Ed. 2006, 45, 916; Angew. Chem. 2006, 118, 930; d) D. N. Dybtsev, M. P. Yutkin, D. G. Samsonenko, V. P. Fedin, A. L. Nuzhdin, A. A. Bezrukov, K. P. Bryliakov, E. P. Talsi, R. V. Belosludov, H. Mizuseki, Y. Kawazoe, O. S. Subbotin, V. R. Belosludov, Chem. Eur. J. 2010, 16, 10348.
- [7] G. Nickerl, A. Henschel, R. Grünker, K. Gedrich, S. Kaskel, Chem. Ing. Tech. 2011, 83, 90.
- [8] a) I. Imaz, M. Rubio-Martinez, J. An, I. Sole-Font, N. L. Rosi, D. Maspoch, *Chem. Commun.* **2011**, *47*, 7287; b) C. Martí-Gastaldo, J. E. Warren, K. C. Stylianou, N. L. O. Flack, M. J. Rosseinsky, *Angew. Chem. Int. Ed.* **2012**, *51*, 11044; *Angew. Chem.* **2012**, *124*, 11206; c) J. Rabone, Y. F. Yue, S. Y. Chong, K. C. Stylianou, J. Bacsa, D. Bradshaw, G. R. Darling, N. G. Berry,

Y. Z. Khimyak, A. Y. Ganin, P. Wiper, J. B. Claridge, M. J. Rosseinsky, *Science* **2010**, *329*, 1053.

- [9] X. Li, C. Chang, X. Wang, Y. Bai, H. Liu, Electrophoresis 2014, 35, 2733.
- [10] a) G. M. Sheldrick, SHELX97, 1997, University of Gttingen, Gttingen, Germany; b) A. L. Spek, J. Appl. Crystallogr. 2003, 36, 7.
- [11] a) M. Y. Masoomi, K. C. Stylianou, A. Morsali, P. Retailleau, D. Maspoch, *Cryst. Growth Des.* **2014**, *14*, 2092; b) B. Bhattacharya, R. Haldar, R. Dey, T. K. Maji, D. Ghoshal, *Dalton Trans.* **2014**, *43*, 2272; c) T. M. McDonald, J. A. Mason, X. Kong, E. D. Bloch, D. Gygi, A. Dani, V. Crocella, F. Giordanino, S. O. Odoh, W. S. Drisdell, B. Vlaisavljevich, A. L. Dzubak, R. Poloni, S. K. Schnell, N. Planas, K. Lee, T. Pascal, L. F. Wan, D. Prendergast, J. B. Neaton, B. Smit, J. B. Kortright, L. Gagliardi, S. Bordiga, J. A. Reimer, J. R. Long, *Nature* **2015**, *519*, 303.
- [12] Z.-X. Zhang, N.-N. Ding, W.-H. Zhang, J.-X. Chen, D. J. Young, T. S. A. Hor, Angew. Chem. Int. Ed. 2014, 53, 4628; Angew. Chem. 2014, 126, 4716.
- [13] a) Y. W. Peng, T. F. Gong, K. Zhang, X. C. Lin, Y. Liu, J. W. Jiang, Y. Cui, *Nat. Commun.* 2014, *5*; b) L. Q. Ma, J. M. Falkowski, C. Abney, W. B. Lin, *Nat. Chem.* 2010, *2*, 838; c) M. Yoon, R. Srirambalaji, K. Kim, *Chem. Rev.* 2012, *112*, 1196; d) K. Tanaka, Y. Kikumoto, N. Hota, H. Takahashi, *New J. Chem.* 2014, *38*, 880; e) Z.-J. Li, J. Yao, Q. Tao, L. Jiang, T.-B. Lu, *Inorg. Chem.* 2013, *52*, 11694; f) K. Tanaka, T. Muraoka, D. Hirayama, A. Ohnish, *Chem. Commun.* 2012, *48*, 8577; g) K. Suh, M. P. Yutkin, D. N. Dybtsev, V. P. Fedin, K. Kim, *Chem. Commun.* 2012, *48*, 513.
- [14] a) A. L. Nuzhdin, D. N. Dybtsev, K. P. Bryliakov, E. P. Talsi, V. P. Fedin, J. Am. Chem. Soc. 2007, 129, 12958; b) M. C. Das, Q. Guo, Y. He, J. Kim, C.-G. Zhao, K. Hong, S. Xiang, Z. Zhang, K. M. Thomas, R. Krishna, B. Chen, J. Am. Chem. Soc. 2012, 134, 8703; c) T. Sawada, A. Matsumoto, M. Fujita, Angew. Chem. Int. Ed. 2014, 53, 7228; Angew. Chem. 2014, 126, 7356.
- [15] D. Bradshaw, T. J. Prior, E. J. Cussen, J. B. Claridge, M. J. Rosseinsky, J. Am. Chem. Soc. 2004, 126, 6106.
- [16] CCDC 1033846 (Co-L-GG), CCDC 1033847 (Co-L-GGbipy_1), CCDC 1033848 (Co-L-GGbipy_2), CCDC 1033849 (Co-L-GGazobipy), and CCDC 1033850 (Co-L-GGazinebipy) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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