

Supporting Information for the Article: Insights on the Formation of Chiral Second Sphere Coordination Complexes with Aromatic Tris Amines: Combined Single Crystal X-ray Crystallography and Molecular Modeling Analyses

Hong-Cui Yu,^a Lei Li^a, Ji Gao^a, Jian Tong^a, Wenxu Zheng,^b Massimo Cametti,^c Antonino Famulari,^c Stefano Valdo Meille,^c Fang Guo^{a*}, and Javier Martí-Rujas^{d*}

^a College of Chemistry, Liaoning University, Shenyang 110036, China.

E-mail: fguo@lnu.edu.cn. Fax: 0086 24 62202380, Tel: 0086 24 62207831

^b College of Chemistry, Fuzhou University, Fuzhou, 350116, China.

^c Dipartimento di Chimica Materiali e Ingegneria Chimica, "Giulio Natta", Politecnico di Milano, Via L. Mancinelli 7, 20131 Milan, Italy.

^d Center for Nano Science and Technology@Polimi, Istituto Italiano di Tecnologia, Via Pascoli 70/3, 20133 Milano, Italy.

Experimental

Materials and methods

All chemicals were commercially purchased and used as received. X-Ray powder diffraction (XRPD) patterns were recorded on a Bruker D8 reflection diffractometer at 40 kV, 100 mA for a Cu-target tube and a graphite monochromator. IR spectra were obtained with Perkin Elmer 100 FT-IR spectrometer using KBr pellets. ¹H NMR spectra were recorded on a Mercury-Plus 300 spectrometer (VARIAN, 300MHz) at 25°C with TMS as the internal reference.

1. Synthesis of ligand

Synthesis of L₁

Anhydrous zinc chloride (25 g), paraformaldehyde (30 g), 1,3,5-trimethyl-benzene (15 ml) and concentrated hydrochloric acid (60 ml) were added and stirred at 95 °C, meanwhile the HCl gas dried with sulfuric acid was blown into the reaction system. After refluxing for 12 h, the mixture was cooled to room temperature to filter the precipitate. Recrystallisation with alcohol and drying in vacuo produced white powder of 1,3,5 – Tris-chloromethyl -2,4,6 – trimethyl-benzene, 16.8 g, yield 60 %. M.p. 173.5 – 174.4 °C, IR (KBr), $\lambda_{\text{max}}/\text{cm}^{-1}$: 2992.812 cm^{-1} (C-H), 651.478 cm^{-1} (C-Cl). ¹H-NMR (CDCl₃, 300 MHz), $\delta(\text{ppm})$: 2.51 (t, 9H, -CH₃), 4.69(s, 6H, -CH₂).

NaHCO₃ 2.6 g, phenylamine (4.0 ml), H₂O (4 ml) and 1,3,5-tris-chloromethyl -2,4,6 – trimethyl-benzene (1.8 g) were added and slowly heated to 95 °C in 0.5 h and then it was refluxed for 4 h. The mixture was then cooled to room temperature to filter the precipitate. Recrystallisation with alcohol and drying in vacuo produced white powder 1.5 g, yield 51%. M.p. 213.5 – 214.7°C. IR(KBr), $\lambda_{\text{max}}/\text{cm}^{-1}$: 3413.066 cm^{-1} (N-H), 3042.590 cm^{-1} (Ar-H), 1601.523 cm^{-1} (Ar-H), 1501.204 cm^{-1} (Ar-H), 751.627 cm^{-1} (Ar-H), 689.942 cm^{-1} (Ar-H). ¹H-NMR (CDCl₃, 300 MHz), $\delta(\text{ppm})$: 2.43 (s, 9H, -CH₃), 3.51(s, 3H, N-H), 4.26 (s, 6H, -CH₂-), 6.68-7.25(m, 15H, Ar-H).

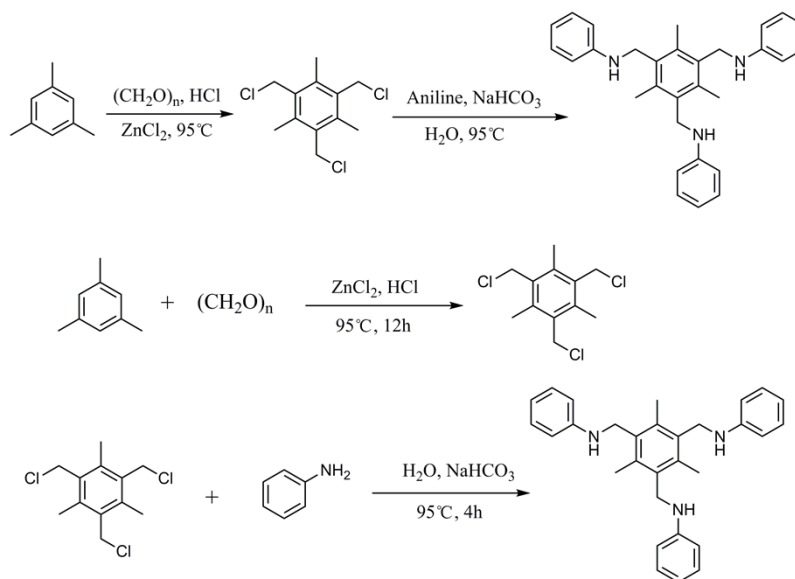


Figure S1. Synthesis of L₁.

Synthesis of L₂

Anhydrous zinc chloride (25 g), paraformaldehyde (30 g), 1,3,5-trimethyl-benzene (15 ml) and concentrated hydrochloric acid (60 ml) were added and stirred at 95 °C, meanwhile the HCl gas dried with sulfuric acid was blown into the reaction system. After refluxing for 12 h, the mixture was cooled to room temperature to filter the precipitate. Recrystallisation with alcohol and drying in vacuo produced white powder of 1,3,5 – Tris-chloromethyl -2,4,6 – trimethyl-benzene, 16.8 g, yield 60 %. M.p. 173.5 – 174.4°C, IR (KBr), $\lambda_{\text{max}}/\text{cm}^{-1}$: 2992.812 cm^{-1} (C-H), 651.478 cm^{-1} (C-Cl). $^1\text{H-NMR}$ (CDCl_3 , 300 MHz), $\delta(\text{ppm})$: 2.51 (t, 9H, -CH₃), 4.69(s, 6H, -CH₂).

K_2CO_3 5.52g, *p*-toluidine (3.37 g), CH_3CN (30 ml) and 1,3,5-tris-chloromethyl -2,4,6 – trimethyl-benzene (2.66 g) were added and slowly heated to 85 °C in 0.5 h and then it was refluxed for 12 h. The mixture was then cooled to room temperature to filter the precipitate. Recrystallisation with alcohol and drying in vacuo produced white powder 2.92 g, yield 61 %. M.p. 204.5 – 205.2°C. IR(KBr), $\lambda_{\text{max}}/\text{cm}^{-1}$: 3407.268 cm^{-1} (N-H), 1615.819 cm^{-1} (Ar-H), 1582.432 cm^{-1} (Ar-H), 1469.381 cm^{-1} (Ar-H), 802.682 cm^{-1} (Ar-H). $^1\text{H-NMR}$ (CDCl_3 , 300 MHz), $\delta(\text{ppm})$: 6.92 (d, 6H, $J = 7.8$ Hz, Ar-H), 6.64 (d, 6H, $J = 7.9$ Hz, Ar-H), 4.93 (s, 3H, -NH), 4.11 (s, 6H, -CH₂-), 2.33 (s, 9H, -CH₃), 2.16 (s, 9H, -CH₃).

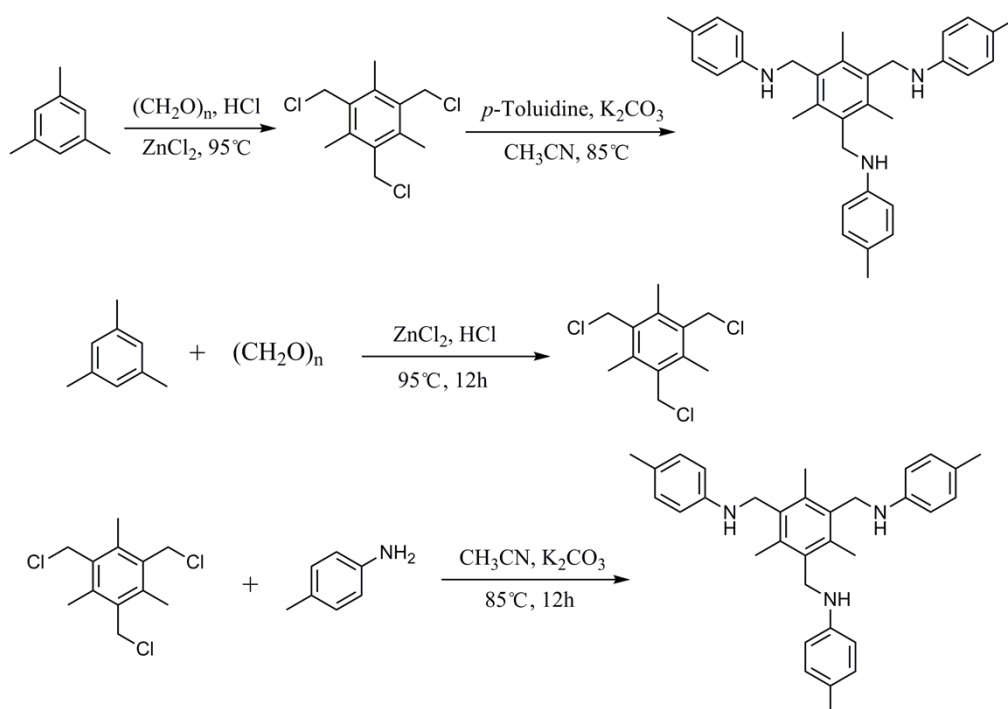


Figure S2. Synthesis of L₂.

Synthesis of L₃

Trimesic acid (20 g, 95 mmol) was suspended in thionyl chloride (60 mL)/DMF (0.369 mL) and refluxed for 4 hours. The reaction mixture was concentrated in vacuo and then dissolved in dichloromethane (2 x 50 mL) and the solution concentrated in vacuo. 1, 3, 5-benzentricarbony trichloride was isolated as a yellow solid (25 g, 98 %).

The solution of 1, 3, 5-benzentricarbony trichloride (2.65 g, 10mmol) in dichloromethane (15 ml) was added slowly over about 30minutes to an ice-cooled stirred solution of aniline (5 ml, 50 mmol) in pyridine (4 ml, 50 mmol) solution. The reaction mixture was stirred for 1 hour at 0 °C then allowed to cool to room temperature for 4 hours. The solid was filtered, washed repeatedly with dichloromethane and water to remove excess aniline and by-product, and dried in vacuo to afford white solid of N¹, N³, N⁵-triphenylbenzene-1, 3, 5-tricarboxamide (3.9 g, 90 %). IR(KBr), $\lambda_{\max}/\text{cm}^{-1}$: 3286.315 cm^{-1} (N-H), 1661.226 cm^{-1} (C=O), 1646.835 cm^{-1} (Ar-H), 1599.467 cm^{-1} (Ar-H), 1492.348 cm^{-1} (Ar-H). ¹H NMR (300 MHz, d₆-DMSO) δ (ppm): 10.60 (s, 3H, -NH), 8.70 (s, 3H, Ar-H), 7.84-7.81 (m, 6H, Ar-H), 7.40-7.37 (t, 6H, $J = 7.9$ Hz, Ar-H), 7.17-7.12 (t, 3H, $J = 7.4$ Hz, Ar-H).

The solution of N¹, N³, N⁵-triphenylbenzene-1, 3, 5-tricarboxamide (4.35 g 10 mmol) in THF (100 mL) was added dropwise to a suspension of lithium aluminium hydride (4.55 g, 120 mmol) in THF (100 mL) at 0 °C, and refluxed for 12 h. After addition of a saturated aqueous sodium sulfate solution, the precipitate was filtered and evaporated in vacuo. A pale yellow solid product (3.2 g, 80%) was obtained after recrystallization of the residues from ethanol. IR(KBr), $\lambda_{\max}/\text{cm}^{-1}$: 3399.412 cm^{-1} (N-H), 1599.247 cm^{-1} (Ar-H), 1507.103 cm^{-1} (Ar-H), 1315.842 cm^{-1} (Ar-H). ¹H NMR (300 MHz, CDCl₃, 298 K) δ (ppm): 7.24 (s, 3H, Ar-H), 6.99-7.01 (t, 6H, $J = 7.9$ Hz, Ar-H), 6.50-6.55 (m, 9H, Ar-H), 6.14 (s, 3H, -NH), 4.19 (s, 6H, -CH₂-).

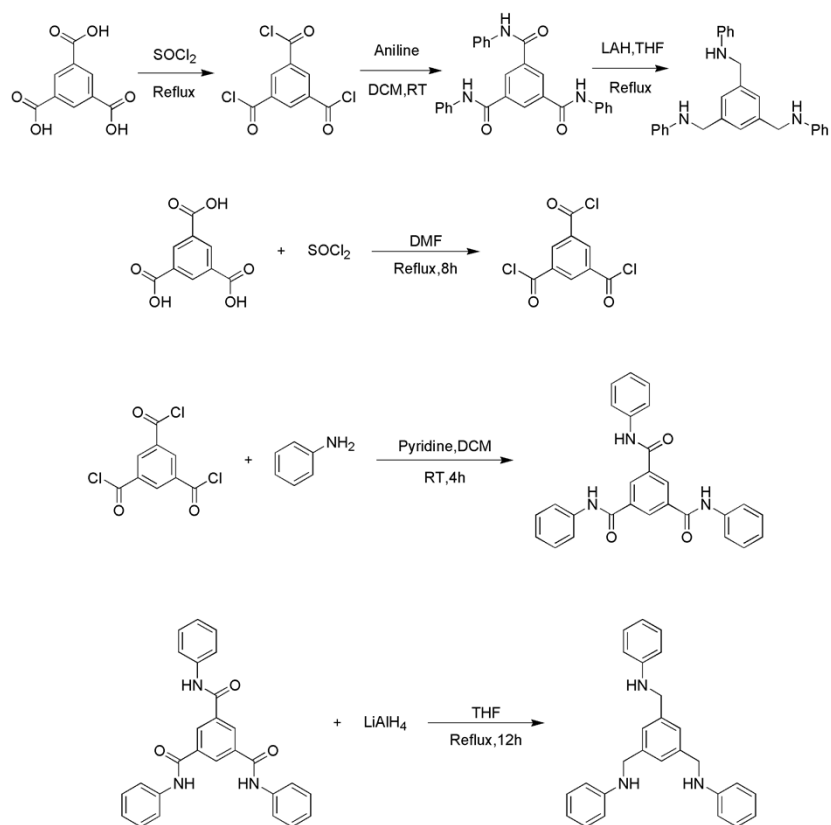


Figure S3. Synthesis of **L₃**.

2. Synthesis of complex 1-5

Single crystals of complexes **1-5** were prepared by mixing ligand **L1** (1 mmol : 436 mg), 3 mL dichloromethane, 15 mL ethanol and 1 mmol $MCl_2 \cdot nH_2O$ ($M = Zn^{II}$, Cd^{II} , Mn^{II} , Co^{II}) (230 mg, 136 mg, 198 mg, 238 mg respectively) / 1 mmol $ZnBr_2$ (327 mg) were placed in a 50 mL Erlenmeyer flask, then 1 mL concentrated HCl / HBr were added and shaken until the contents were dissolved. The flask was allowed to stand for *ca.* 2-3 days at room temperature, giving rise to high quality crystals with tetrahedral morphology suitable for single crystal X-ray diffraction.

3. Synthesis of complexes 6-9

Single crystals of complexes **6-9** were prepared by mixing ligand **L²** (1 mmol : 477 mg), 3 mL dichloromethane, 15 mL ethanol and 1 mmol $MCl_2 \cdot nH_2O$ ($M = Cd^{II}$, Co^{II} , Hg^{II} , Zn^{II}) (230 mg, 238 mg, 272 mg, 136 mg respectively) in a 50 mL Erlenmeyer flask, then 0.15 mL concentrated HCl was added and shaken until the contents were dissolved. The flask was allowed to stand for 3-5 days at room

temperature, giving rise to high quality crystals with tetrahedral morphology suitable for single crystal X-ray diffraction.

4. Synthesis of complex 10

Single crystal of complex **10** was prepared by mixing ligand **L**³ (1 mmol : 477 mg), 6 mL dichloromethane, 15 mL ethanol and ZnCl₂ (2 mmol, 272 mg) in a 50 mL Erlenmeyer flask, then 0.15 mL concentrated HCl was added and shaken until the contents were dissolved. The flask was allowed to stand for 2-3 days at room temperature, giving rise to high quality colorless needlelike crystals suitable for single crystal X-ray diffraction.

4. Synthesis of complex 11-12

L¹ (1 mmol : 436 mg) and 1 mmol MCl₂·nH₂O (M = Cd^{II}, Cu^{II}) (230 mg, 170 mg respectively) were placed in an agate mortar, then 0.1 mL ethanol and 0.1 mL concentrated HCl were added. The contents were ground for 30min at room temperature. The mixture was dissolved in 5 mL dichloromethane and 15 mL ethanol in a 50mL Erlenmeyer flask, then 0.15 mL concentrated HCl was added. The flask was allowed to stand for 3-4 days at room temperature, giving rise to high quality colorless block crystals suitable for single crystal X-ray diffraction.

Quantum Mechanical calculations: methods

Density functional theory (DFT) approaches have been employed. The PBE (Perdew–Burke–Ernzerhof)¹ exchange-correlation functions, have been used both for gas and solid phases (*i.e.*, under periodical conditions) and, for the sake of consistency, all the calculations were accomplished by the DMol³ software.²

A combination of numerical double- ζ quality basis set (not including or including polarization functions on all atoms, *i.e.*, DND and DNP) and an effective core potential for the metal atoms was adopted. In all the calculations, we assumed experimental X-ray determined unit cells and geometries for heavy atoms while X–H

bond lengths were optimised. A similar computational approach was proved to be adequate in a number of cases such as large supramolecular complexes,³ systems containing charged particles⁴ and crystalline phases of thiophene based oligomers and polymers.⁵ The effects of inter and intermolecular interactions have been accounted for by using the well-known Grimme scheme in the framework of a DFT-D approach.⁶

Table S1. Crystallographic data and structural refinement for ligand **L₁**.

L₁	
Chem. form	C ₃₀ H ₃₃ N ₃
Form wt.	435.6
Crystal system	100(2)
Space group	C2
Z	4
a(Å)	20.952(4)
b(Å)	5.6060(11)
c(Å)	20.275(4)
α(°)	90
β(°)	95.697(12)
γ(°)	90
V(Å ³)	2369.7(8)
D _x (g.cm ⁻³)	1.156
F(000)	844
R _{int}	0.0332
R _f /wR _f	0.0343/0.0867
s	1.026

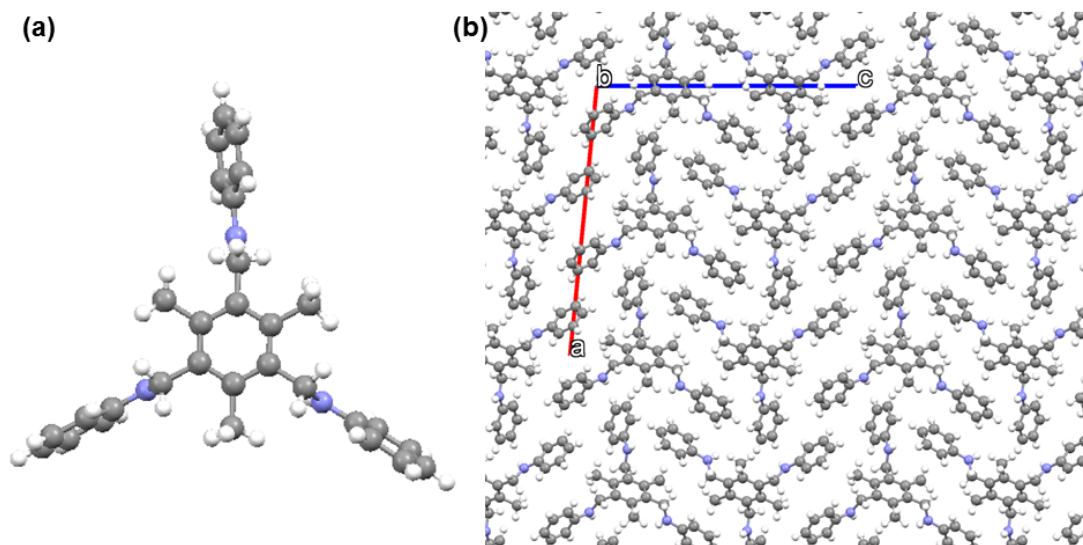


Figure S4. (a) Crystal structure of **L₁**. (b) Packing along the *b*-axis.

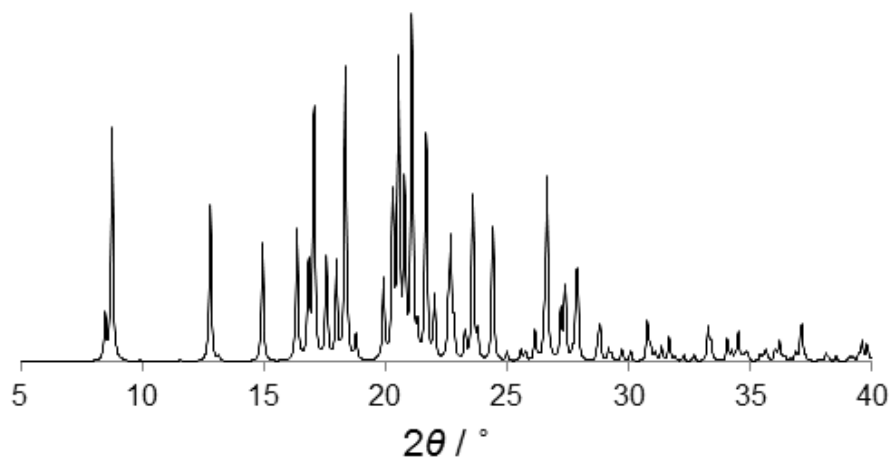


Figure S5. Simulated XRPD of L₁.

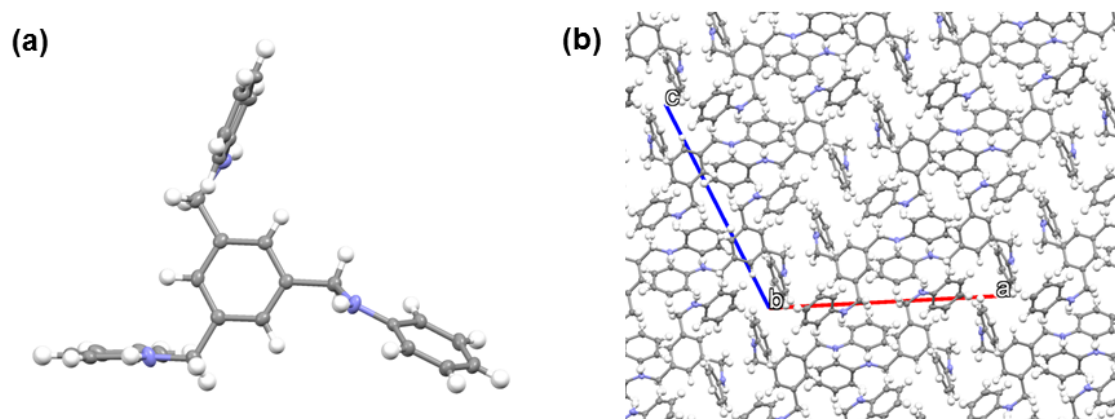


Figure S6. (a) Crystal structure of L₃. (b) Packing along the *b*-axis.

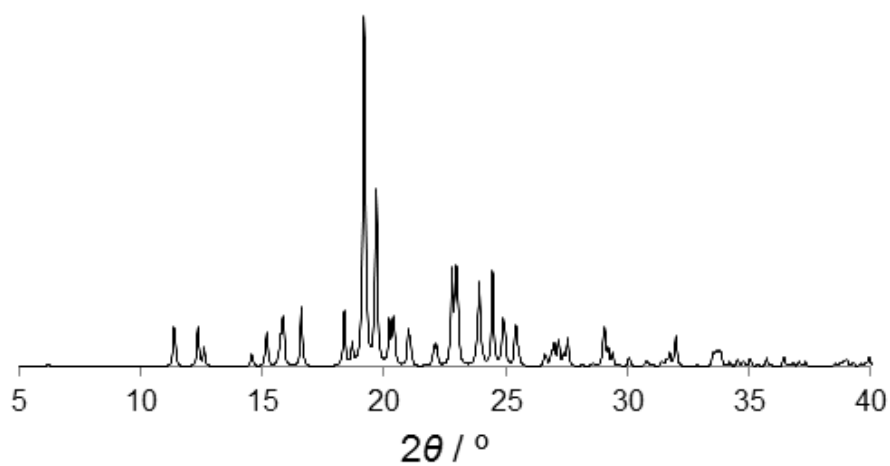


Figure S7. Simulated XRPD of L₃.

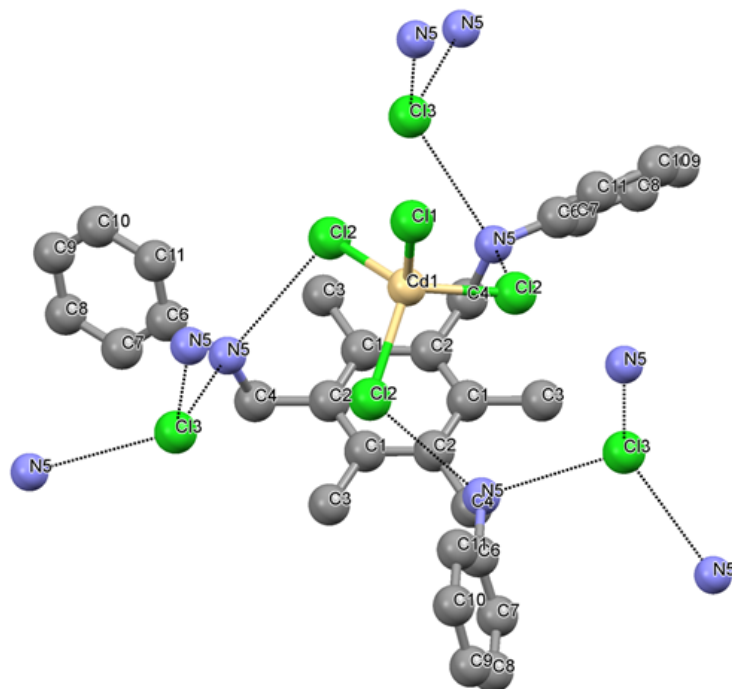


Figure S8. Crystal structure of **2**.

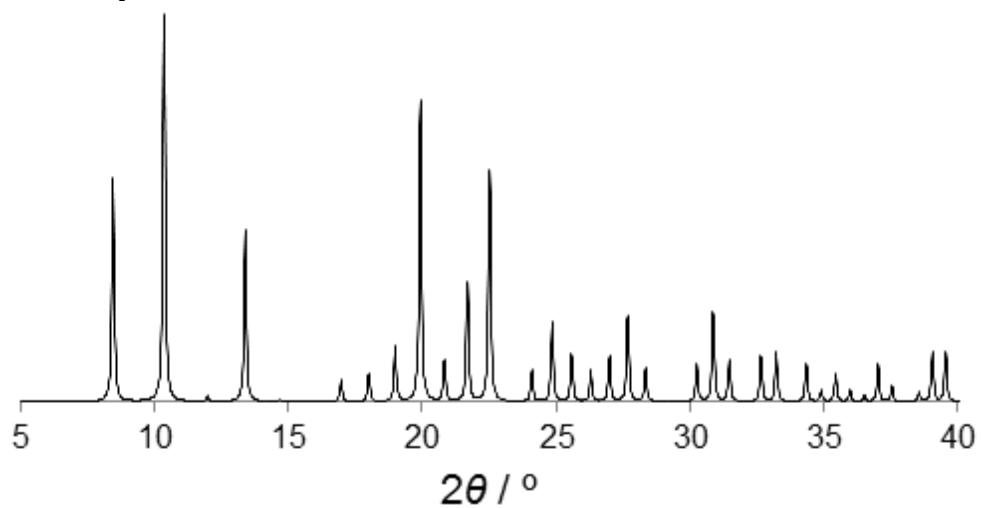


Figure S9. Simulated XRPD of **2** adduct.

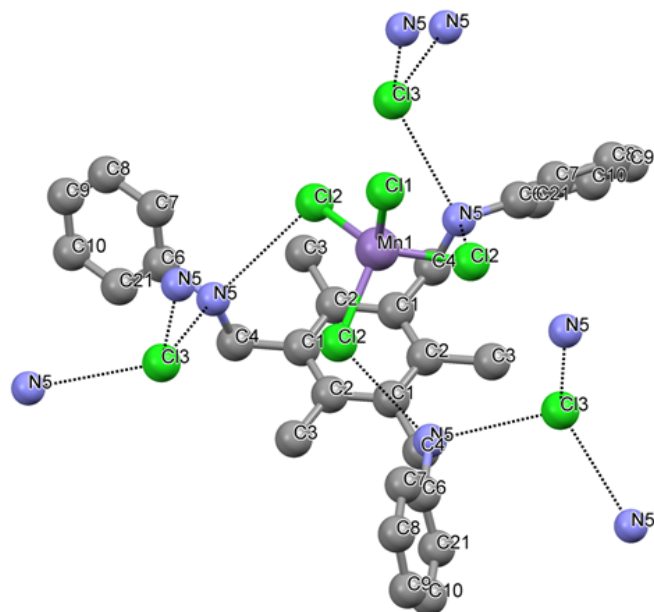


Figure S10. Crystal structure of **3**.

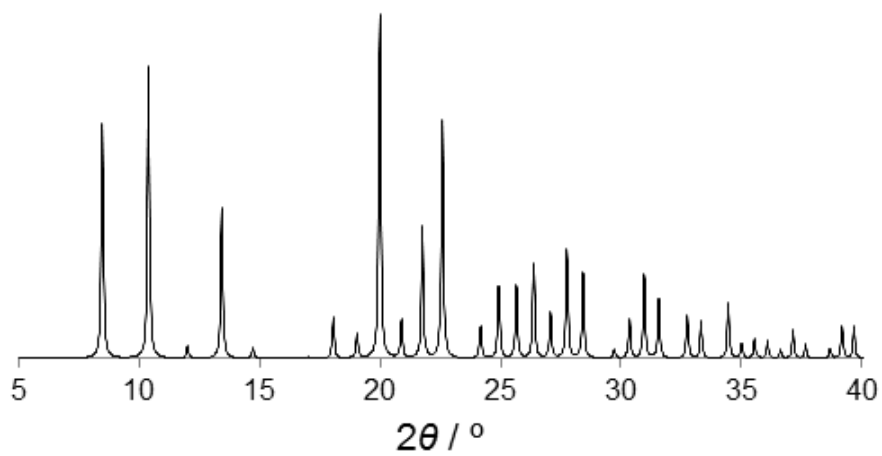


Figure S11. Simulated XRPD of **3** adduct.

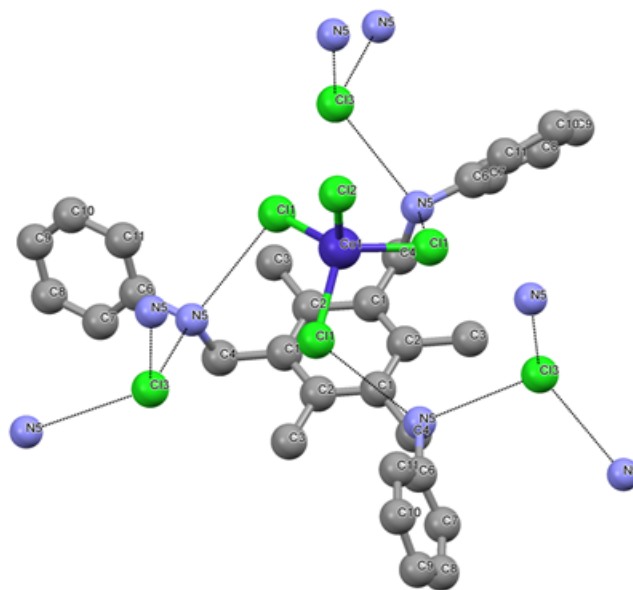


Figure S12. Crystal structure of **4**.

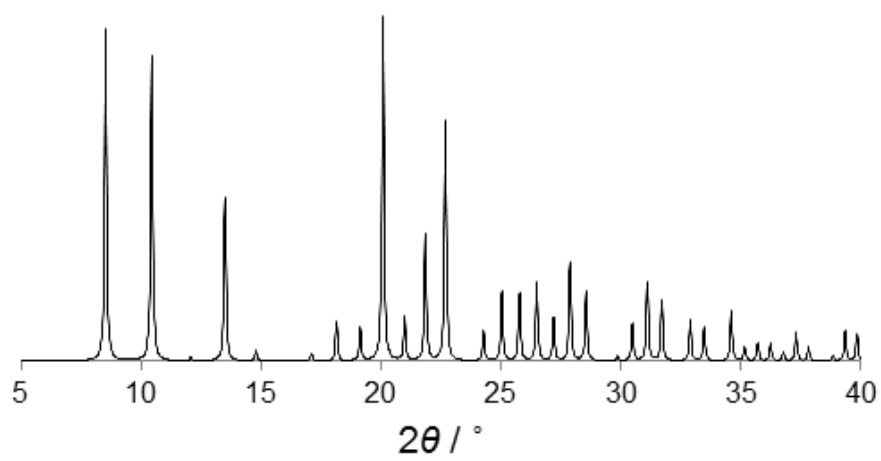


Figure S13. Simulated XRPD of **4** adduct.

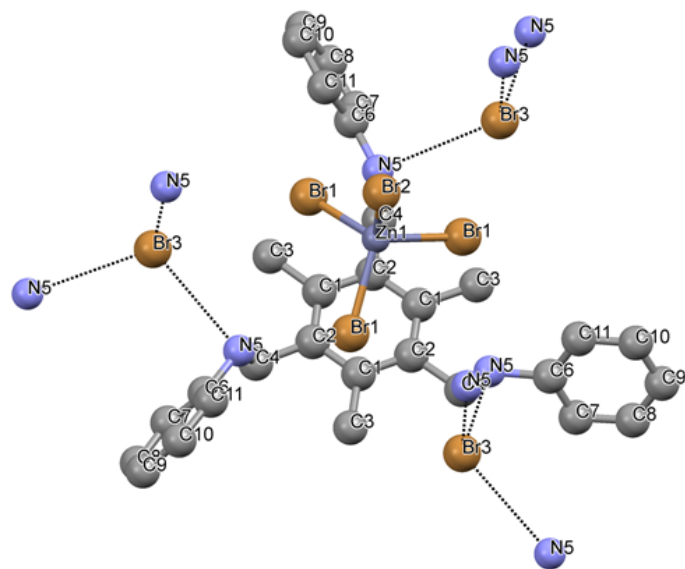


Figure S14. Crystal structure of **5**.

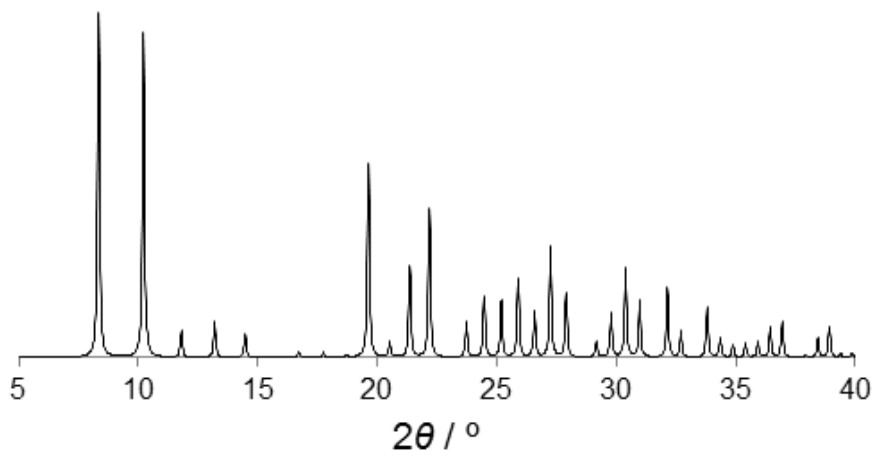


Figure S15. Simulated XRPD of **5** adduct.

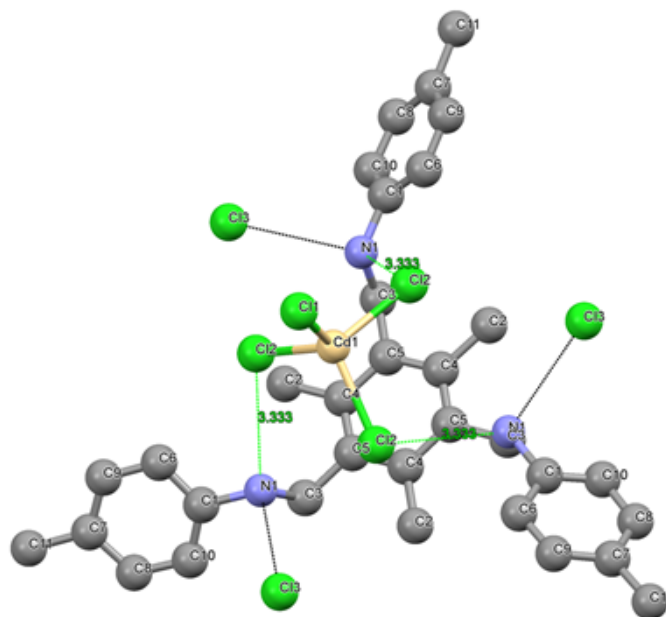


Figure S16. Crystal structure of **6**.

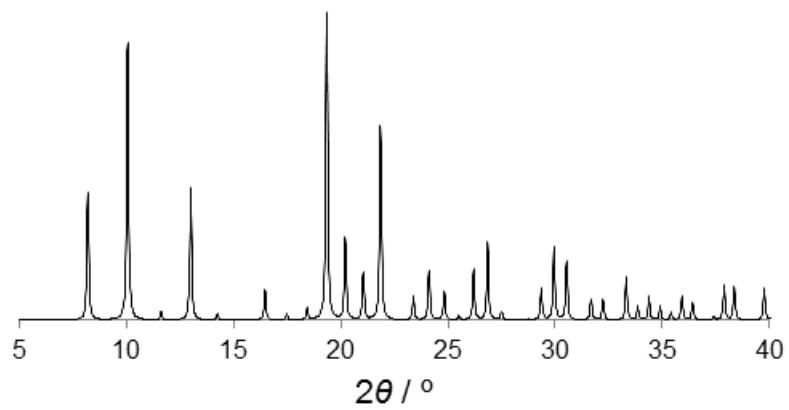


Figure S17. Simulated XRPD of **6** adduct.

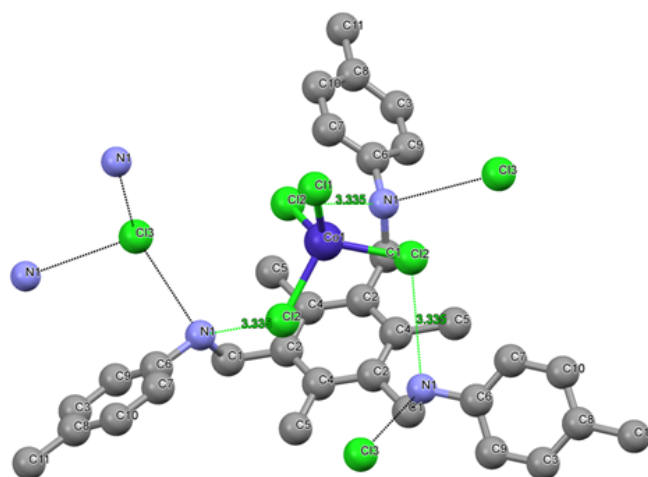


Figure S18. Crystal structure of **7**.

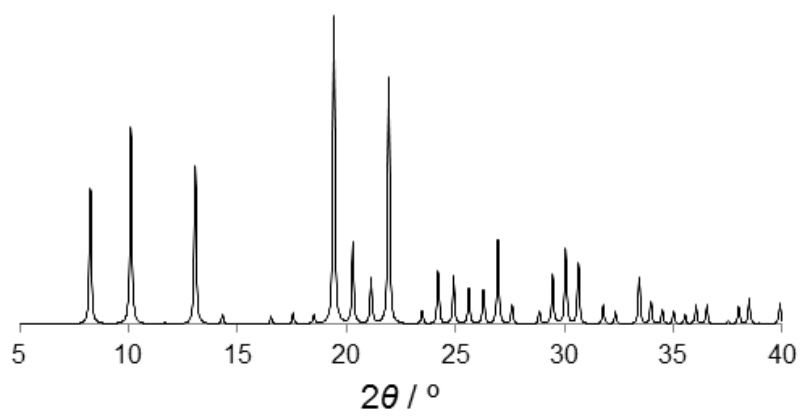


Figure S19. Simulated XRPD of **7** adduct.

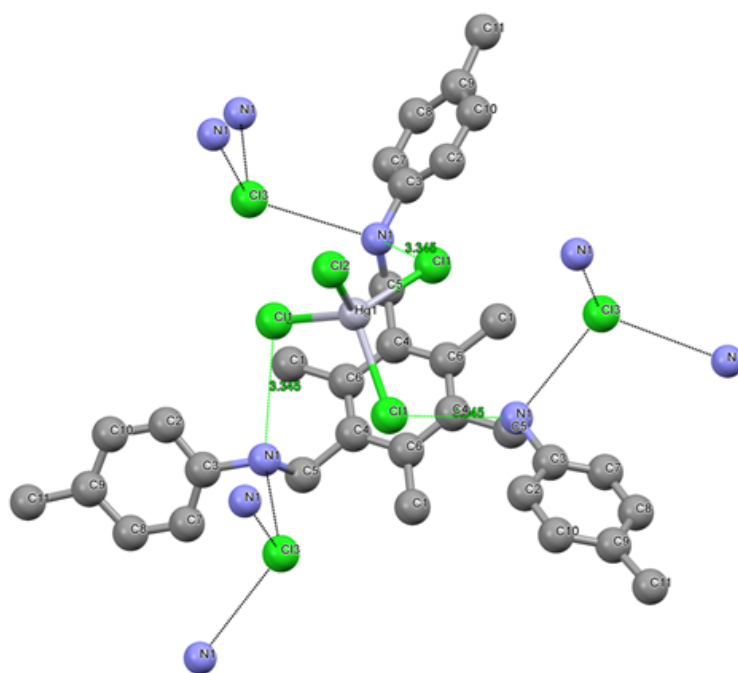


Figure S20. Crystal structure of **8**.

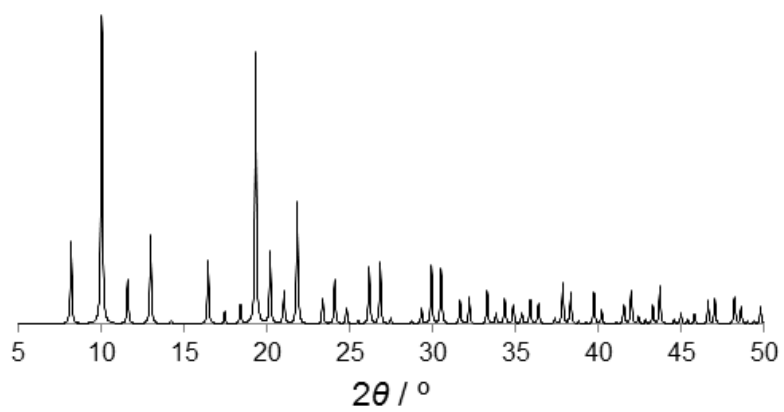


Figure S21. Simulated XRPD of **8** adduct.

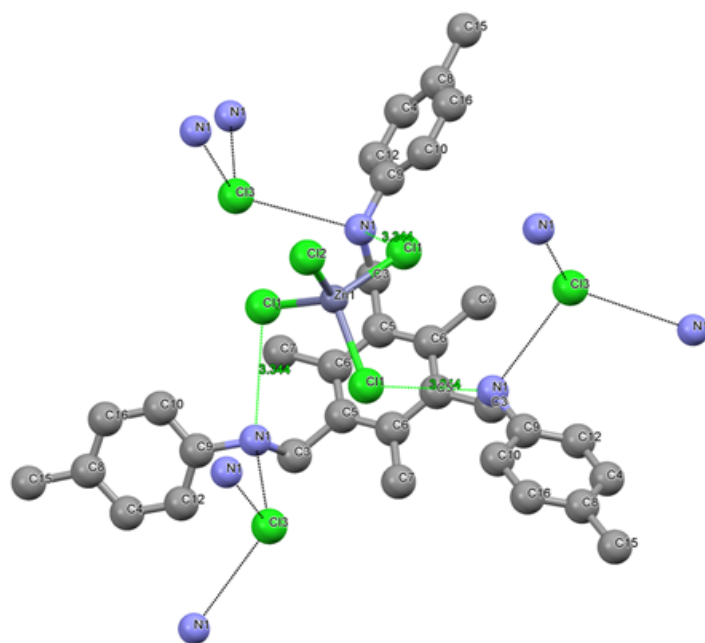


Figure S22. Crystal structure of **9**.

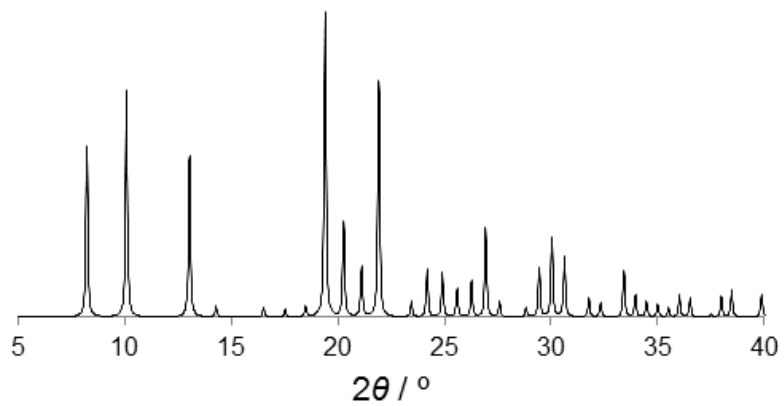


Figure S23. Simulated XRPD of **9** adduct.

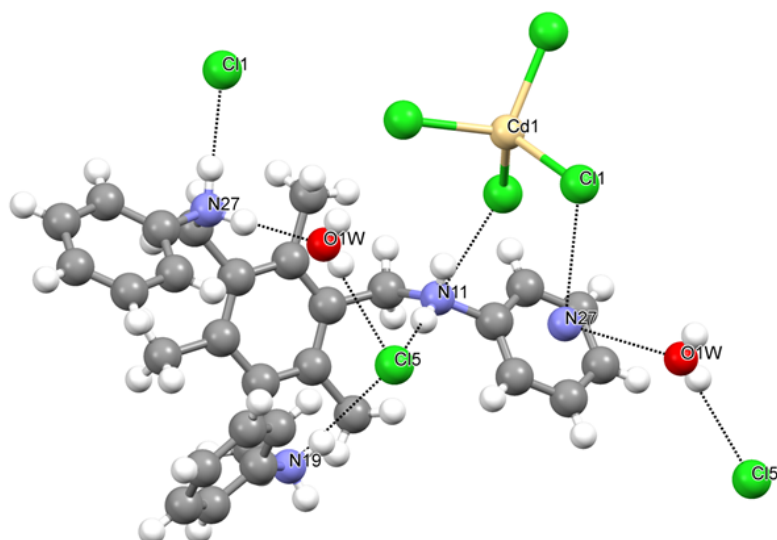


Figure S24. Crystal structure of achiral structure **12** using L_1 .

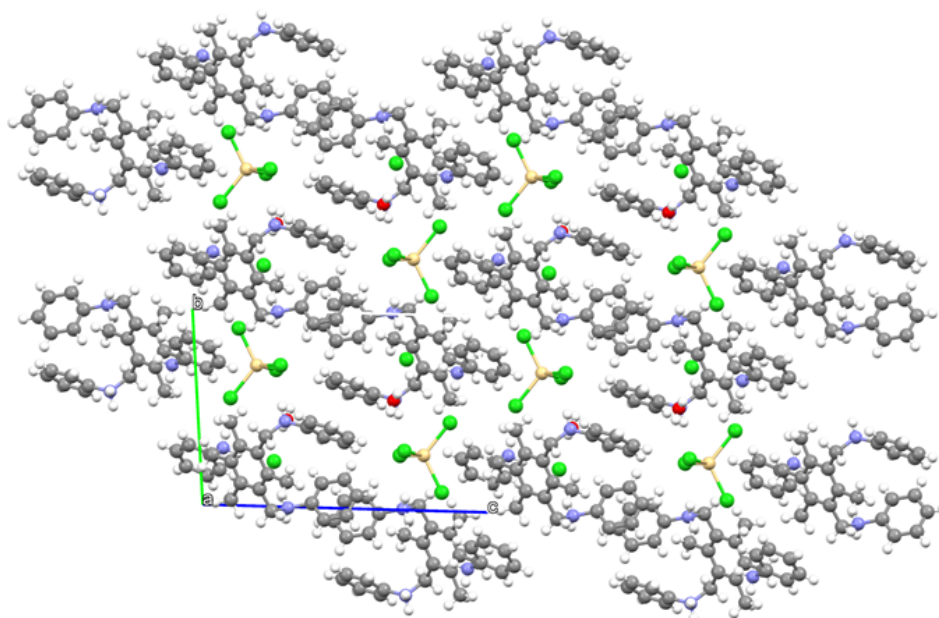


Figure S25. Crystal structure of achiral structure **12** showing the molecular packing along the a -axis.

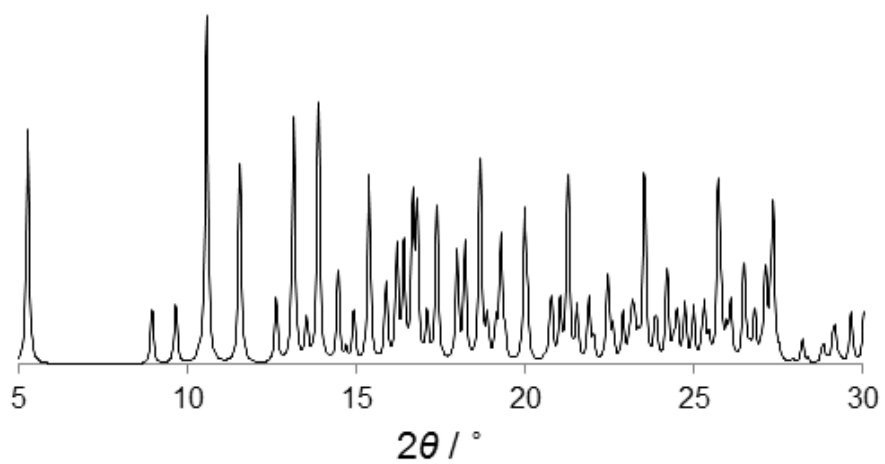


Figure S26. Simulated XRPD of SSC adduct **12**.

Table S1. Crystallographic data of SSCs 1-12.

Crystals	1	2	3	4	5	6
Empirical formula	C ₃₀ H ₃₆ N ₃ ZnCl ₅	C ₃₀ H ₃₆ N ₃ CdCl ₅	C ₃₀ H ₃₆ N ₃ MnCl ₅	C ₃₀ H ₃₆ N ₃ CoCl ₅	C ₃₀ H ₃₆ N ₃ ZnBr ₅	C ₃₃ H ₄₂ N ₃ CdCl ₅
Formula weight	681.16	728.28	670.81	674.80	903.51	770.36
Dimensions(mm)	0.18×0.20× 0.28	0.30×0.24× 0.18	0.31×0.27× 0.20	0.33×0.30× 0.22	0.19×0.17× 0.12	0.16×0.14× 0.11
Temperature (K)	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)
Crystal system	Cubic	Cubic	Cubic	Cubic	Cubic	Cubic
Space group	P2 ₁ 3	P2 ₁ 3	P2 ₁ 3	P2 ₁ 3	P2 ₁ 3	P2 ₁ 3
Z	4	4	4	4	4	4
a(Å)	14.6693(4)	14.759(2)	14.7135(6)	14.6540(12)	14.9853(18)	15.1987(19)
b(Å)	14.6693(4)	14.759(2)	14.7135(6)	14.6540(12)	14.9853(18)	15.1987(19)
c(Å)	14.6693(4)	14.759(2)	14.7135(6)	14.6540(12)	14.9853(18)	15.1987(19)
α(deg)	90	90	90	90	90	90
β(deg)	90	90	90	90	90	90
γ(deg)	90	90	90	90	90	90
V(Å ³)	3156.66(15)	3214.9(8)	3185.3(2)	3146.8(4)	3365.1(7)	3510.9(8)
D _x (Mg.cm ⁻³)	1.433	1.505	1.399	1.392	1.783	1.457
μ(mm ⁻¹)	1.226	1.119	0.858	0.994	6.691	1.029
F(000)	1408	1480	1388	1336	1768	1576
R _{int}	0.0288	0.0213	0.0244	0.0294	0.0526	0.0269
Total reflns	19823	20151	20015	19782	21185	21889
Unique reflns	2430	2466	2466	2428	2628	2707
Obsd reflns	2303	2399	2357	2283	2206	2621
s	1.024	1.089	1.019	0.987	1.054	1.101
R _f /wR _f	0.0255/0.0631	0.0194/0.0507	0.0262/0.0674	0.0264/0.0642	0.0309/0.0606	0.0234/0.0537
All data R _f /wR _f	0.0279/0.0644	0.0203/0.0513	0.0276/0.0683	0.0292/0.0660	0.0442/0.0646	0.0250/0.0546
CCDC number	1406456	1406455	1406457	1406458	1406459	1406460

Crystals	8	7	9	10	11	12
Empirical formula	C ₃₃ H ₄₂ N ₃ HgCl ₅	C ₃₃ H ₄₂ N ₃ CoCl ₅	C ₃₃ H ₄₂ N ₃ ZnCl ₅	C ₂₇ H ₃₀ N ₃ ZnCl ₅	C ₃₀ H ₃₈ N ₃ OCdCl ₅	C ₃₀ H ₃₈ N ₃ OCuCl ₅
Formula weight	858.51	716.83	723.34	635.02	746.29	697.43
Dimensions(mm)	0.25×0.24× 0.18	0.22×0.21× 0.16	0.23×0.19× 0.14	0.20×0.18× 0.16	0.25×0.20× 0.08	0.32×0.25× 0.23
Temperature (K)	293(2)	293(2)	293(2)	296(2)	293(2)	293(2)
Crystal system	Cubic	Cubic	Cubic	Triclinic	Triclinic	Triclinic
Space group	P2 ₁ 3	P2 ₁ 3	P2 ₁ 3	P-1	P-1	P-1
Z	4	4	4	3	2	2
a(Å)	15.208(3)	15.1477(8)	15.155(4)	10.428(8)	8.5477(7)	8.5878(19)
b(Å)	15.208(3)	15.1477(8)	15.155(4)	11.382(8)	11.5561(9)	11.611(3)
c(Å)	15.208(3)	15.1477(8)	15.155(4)	14.421(11)	16.7666(13)	16.134(4)
α(deg)	90	90	90	86.257	94.5640(10)	93.826(3)
β(deg)	90	90	90	74.387	90.6690(10)	92.064(3)
γ(deg)	90	90	90	62.935	92.3010(10)	90.772(3)
V(Å ³)	3517.4(12)	3475.7(3)	3480.7(16)	1464.6(18)	1649.4(2)	1603.9(7)
D _x (Mg.cm ⁻³)	1.616	1.358	1.380	1.433	1.501	1.442
μ(mm ⁻¹)	4.782	0.905	1.116	1.410	1.095	1.126
F(000)	1692	1468	1504	651	758	720
R _{int}	0.0572	0.0342	0.0308	0.0143	0.0114	0.0135
Total reflns	21666	21842	21634	9145	10426	9924
Unique reflns	2696	2697	2687	6446	7329	6974
Obsd reflns	2471	2440	2473	5568	6416	5460
s	1.092	1.011	1.048	1.026	1.003	0.979
R _f /wR _f	0.0323/0.0759	0.0310/0.0814	0.0260/0.0615	0.0338/0.0847	0.0406/0.0923	0.0492/0.1238
All data R _f /wR _f	0.0364/0.0773	0.0357/0.0844	0.0298/0.0631	0.0400/0.0881	0.0469/0.0962	0.0641/0.1336
CCDC number	1406462	1406461	1406463	1406464	1406465	1406466

References

¹ Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.*, **1996**, *77*, 3865. Ibid. E, *Phys. Rev. Lett.*, **1997**, *78*, 1396.

² Delley, B. *J. Chem. Phys.* **2000**, *113*, 7756; Materials Studio and DMOL³ are Accelrys Inc. products (see www.accelrys.com).

³ (a) Kolokoltsev, Y.; Amelines-Sarria, O.; Gromovoy, T. Y.; Basiuk, V. A. *J. Comput. Theor. Nanosci.* **2010**, *7*, 1095; (b) Amelines-Sarria, O.; Kolokoltsev, Y.; Basiuk, V. A. *J. Comput. Theor. Nanosci.* **2010**, *7*, 1996; (c) Basiuk, V. A.; Amelines-Sarria, O.; Kolokoltsev, Y. *J. Comput. Theor. Nanosci.* **2010**, *7*, 2322; (d) Basiuk, V. A. *Int. J. Quantum Chem.* **2011**, *15*, 4197;

⁴ (a) Yu, G.; Yin, S.; Liu, Y.; Shuai, Z.; Zhu, D. *J. Am. Chem. Soc.* **2003**, *125*, 14816; (b) Guo, F.; Zhang, M. Q.; Famulari, A.; Martí-Rujas, J. *CrystEngComm*, **2013**, *15*, 6237; (c) Maccaroni, E.; Malpezzi, L.; Famulari, A.; Masciocchi, N. *J. Pharmaceut. Biomed. Anal.* **2012**, *60*, 65-

⁵ (a) Famulari, A.; Raos, G.; Baggioli, A.; Casalegno, M.; Po, R.; Meille, S.V. *J. Phys. Chem. B*, **2012**, *116*, 14504; (b) Casalegno, M.; Baggioli, A.; Famulari, A.; Meille, S. V.; Nicolini, T.; Po, R.; Raos, G. 2012, 02002-1 02002-8, Materials for organic photovoltaics: insights from detailed structural models and molecular simulations, EPJ WEB OF CONFERENCES, ISSN 2100-014X, DOI:10.1051/epjconf/20123302002; (c) Nicolini, T.; Famulari, A.; Gatti, T.; Martí-Rujas, J.; Villafiorita Monteleone, F.; Canesi, E. V.; Botta, C.; Parisini, E.; Meille, S.

V.; Bertarelli, C. *J. Phys. Chem. Lett.*, 2014, **5**, 2171–2176..

⁶ (a) Grimme, S. *J. Chem. Phys.* **2006**, *124*, 34108; (b) Baggioli, A.; Meille, S. V.; Raos, G. ; Po, R.; Brinkmann, M.; Famulari, A. *Int. J. Quantum Chem.* **2013**, *113*, 2154; (b) Baggioli, A.; Famulari, A. *Phys. Chem. Chem. Phys.*, **2014**,*16*, 3983-3994.