Supplementary Information

Silver(I) coordination polymers with 3,3',5,5'-tetrasubstituted 4,4'-bipyridine ligands: towards new porous chiral materials

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I. Analytical data

$[Ag(L3)(NO_3)(H_2O)]_n$ (C3). Anal. Calcd for $C_{10}H_6AgBr_2I_2N_3O_4$: C, 15.94; H, 0.80; N, 5.58. Found: C, 15.96; H, 0.73; N, 5.52.

$[Ag(L4)(NO_3)(H_2O)]_n$ (C4). Anal. Calcd for $C_{10}H_6AgCl_2I_2N_3O_4$: C, 18.07; H, 0.91; N, 6.32. Found: C, 18.13; H, 0.94; N, 6.36.

$[Ag(rac\text{-}L5)_2(NO_3)]_n$ (C5a). Anal. Calcd for $C_{48}H_{36}AgBr_4N_5O_7$: C, 47.17; H, 2.97; N, 5.73. Found: C, 47.43; H, 2.95; N, 5.77. FTIR: 3454m, 2960w, 2929w, 2836w, 1609s, 1572w, 1509s, 1463w, 1416m, 1400m, 1384s, 1352m, 1296m, 1252s, 1204w, 1179s, 1163m, 1112w, 1043m, 895w, 831m, 825m, 769m, 751w, 724w, 684w, 661w, 643w, 607m, 588w, 577m, 537w cm^{-1}.

$\{[Ag_2((M)\text{-}L5)_2(NO_3)_2]_2 \cdot i\text{PrOH}\}_n$ (C5b). Anal. Calcd for $C_{48}N_6O_{10}H_{36}Br_4Ag_2\ C_3H_8O$: C, 42.18; H, 3.05; N, 5.79. Found: C, 41.99; H, 3.18; N, 5.66. FTIR: 3446m, 3072w, 2965w, 2930w, 2836w, 1608s, 1572w, 1507s, 1462m, 1420s, 1385s, 1308s, 1287s, 1253s, 1214m, 1184s,1164s, 1111w, 1049m, 1019m, 953w, 897w, 831m, 821m, 771m, 750w, 724w, 697w, 656w, 643w, 607m, 590m, 580m, 532w cm^{-1}.

II. Crystallographic data

Table S1. Crystallographic data for the complexes built from achiral bipyridines **L1** and **L2**.

	C1a	**C1a'**	**C1b**	**C1c**	**C2a**	**C2b**	**C2c**
CCDC deposition number	1439676	1439682	1439678	1439679	1439677	1439680	1439681
Formula	$C_{10}N_2H_4Cl_4$ $AgNO_3$	$(C_{10}N_2H_4Cl_4)_3$ $AgNO_3$	$(C_{10}N_2H_4Cl_4)_5$ $AgBF_4$	$(C_{10}N_2H_4Cl_4)_2$ $(AgCF_3SO_3)_2$ EtOH	$C_{10}N_2H_4Br_4$ $AgNO_3$	$C_{10}N_2H_4Br_4$ $AgBF_4$	$C_{10}N_2H_4Br_4$ $AgCF_3SO_3$
Temperature (K)	110	110	110	110	110	110	110
Space group	*P* $2_1/c$	*P* $2_1/c$	*P* 2/*c*	*P* -1	*P* $2_1/c$	*P* $2_1/c$	*C m c a*
Z	4	4	2	2	4	4	8
a (Å)	7.1747(1)	13.8267(1)	11.53665(13)	12.2195(2)	7.40984(6)	8.32960(10)	15.18790(13)
b (Å)	11.7418(1)	11.6089(1)	7.59398(10)	12.5892(2)	12.03342(9)	12.74030(10)	22.0564(17)
c (Å)	16.5245(1)	25.4608(3)	35.9275(4)	13.8909(2)	16.56423(14)	14.5548(2)	11.44450(10)
α (°)	90.00	90.00	90.00	88.310(2)	90.00	90.00	90.00
β (°)	92.237(1)	106.841(1)	95.6775(10)	78.533(2)	94.4891(7)	92.6540(10)	90.00
γ (°)	90.00	90.00	90.00	61.721(2)	90.00	90.00	90.00
V ($Å^3$)	1391.03(2)	3911.51(6)	3132.14(6)	1839.10(5)	1472.43(2)	1542.92(3)	3833.8(2)
Wavelength (Å)	0.71073	0.71073	1.54184	1.54184	0.71073	0.71073	1.54184
R_{int}	0.0209	0.0249	0.0215	0.0246	0.0320	0.0283	0.0162
No. reflections / No. parameters	6656 / 190	16052 / 478	6565 / 389	7580 / 480	7057 / 190	7387 / 199	2089 / 120
$(\sin\theta/\lambda)_{max}$ ($Å^{-1}$)	0.83	0.79	0.63	0.63	0.83	0.83	0.63
R_1	0.0254	0.0343	0.0277	0.0213	0.0301	0.0369	0.0205
wR_2	0.0459	0.0657	0.0681	0.0528	0.0578	0.0662	0.0551
g.o.f.	1.036	1.087	1.137	1.048	1.020	1.057	1.059
ρ_{min} / ρ_{max} (e. $Å^{-3}$)	-0.585 / 0.697	-1.134 / 1.168	-0.440 / 0.538	-0.712 / 0.606	-1.446 / 1.371	-1.267 / 1.349	-1.115 / 1.364

Table S2. Crystallographic data for the complexes built from chiral racemic bipyridines **L3** and **L4**.

	C3	**C4**
CCDC deposition number	1439684	1439686
Formula	$C_{10}N_2H_4Br_2I_2$ $AgNO_3$ H_2O	$C_{10}N_2H_4Cl_2I_2$ $AgNO_3$ H_2O
Temperature (K)	110	110
Space group	*C* 2/*c*	*P* -1
Z	8	2
a (Å)	21.9475(6)	7.04040(10)
b (Å)	7.8051(2)	11.1885(2)
c (Å)	19.9629(5)	11.46640(10)
α (°)	90.00	69.9870(10)
β (°)	107.285(3)	76.9540(10)
γ (°)	90.00	75.0360(10)
V ($Å^3$)	3265.25(15)	810.46(2)
Wavelength (Å)	1.54184	0.71073
R_{int}	0.0242	0.0226
No. reflections / No. parameters	3414 / 214	8288 / 213
$(\sin\theta/\lambda)_{max}$ ($Å^{-1}$)	0.63	0.85
R_1	0.0383	0.0331
wR_2	0.0905	0.0602
g.o.f.	1.218	1.233
ρ_{min} / ρ_{max} (e. $Å^{-3}$)	-1.651 / 1.774	-1.719 / 1.476

Table S3. Crystallographic data for the complexes built from chiral bipyridines **L5** (racemic and (*M*)-enantiomer).

	C5a	**C5b**
CCDC deposition number	1439683	1439685
Formula	$(C_{24}N_2O_2H_{18}Br_2)_2$ $AgNO_3$	$(C_{24}N_2O_2H_{18}Br_2$ $AgNO_3)_2$ iPrOH
Temperature (K)	110	110
Space group	*P* $2_1/c$	*P* 2_1
Z	4	4
a (Å)	11.5735(1)	11.40500(10)
b (Å)	30.6737(2)	11.11900(10)
c (Å)	13.4661(1)	23.0313(3)
α (°)	90.00	90.00
β (°)	108.102(1)	97.9270(10)
γ (°)	90.00	90.00
V ($Å^3$)	4543.88(6)	2892.74(5)
Wavelength (Å)	1.54184	0.71073
R_{int}	0.0256	0.0407
No. reflections / No. parameters	9532 / 601	16603 / 666
$(\sin\theta/\lambda)_{max}$ ($Å^{-1}$)	0.63	0.70
R_1	0.0272	0.0619
wR_2	0.0632	0.1482
g.o.f.	1.061	1.169
ρ_{min} / ρ_{max} (e. $Å^{-3}$)	-1.576 / 1.522	-3.356 / 1.729

III. Figures

Fig. S1. Molecular graph obtained from the topological analysis of the electron density issued from the DFT calculation on complex **C1a**; a cluster of two Ag^{+}, two NO_3^{-} and four ligands **L1** were considered, centered on one silver atom (light grey sphere). Bond critical points are depicted as small light green spheres, and electron density values are given in atomic units for the Ag···N,O,Cl bonds. Some atoms (large spheres) were omitted for clarity. Color scheme: Ag: light grey; C: grey; O: red; N:blue; H:white; Cl: green. The bond path between Ag^{+} and Cl is depicted as a dashed line.

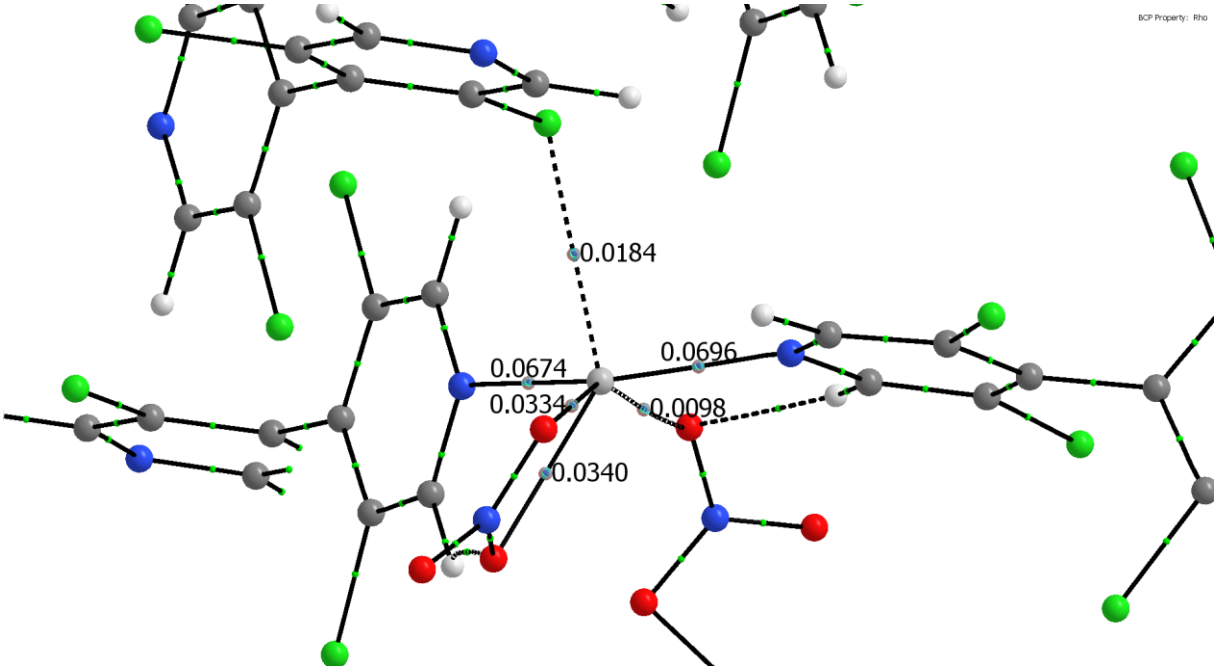


Fig S2. Crystal packing in **C2a** viewed along the bipyridine-silver chains [201] direction. The (10-2) planes formed by chains interacting through nitrate anions are shown as dotted-dashed lines and Ag···Br interactions are displayed as dashed lines.

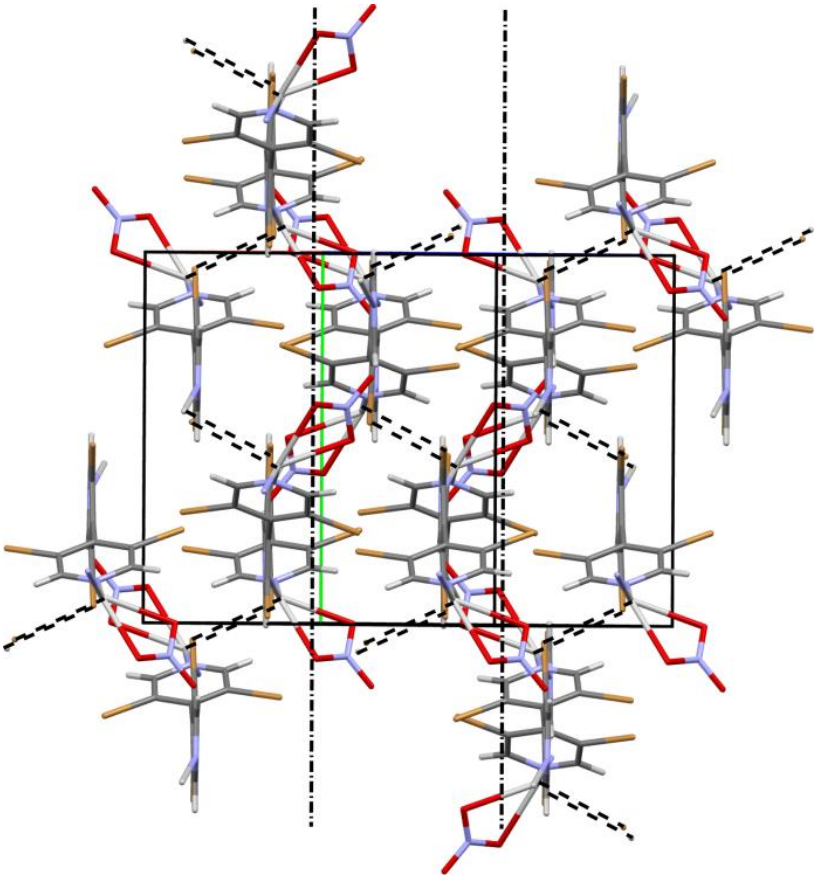
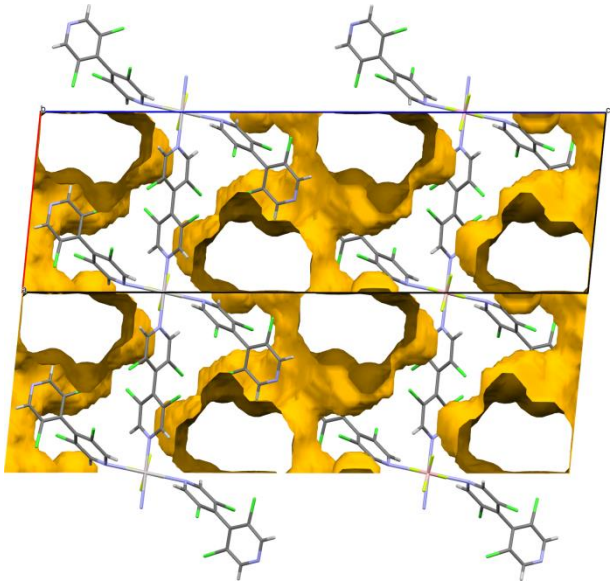
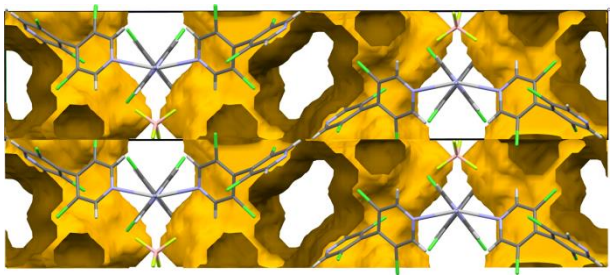


Fig. S3. Views of the silver tetrachloro-4,4’-bipyridine tetrafluoroborate complex **C1b** along (a) [010] and (b) [100]



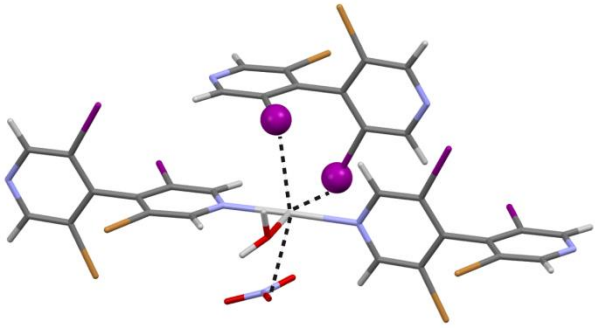
(a)



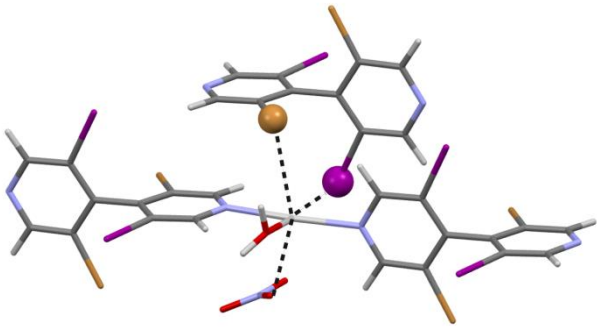
(b)

Fig. S4. Coordination around silver for the four structures considered for periodic DFT calculation on complex **C4**. From top to bottom: (i), (ii); (iii) and (iv). Color scheme: bromine: brown; iodine: magenta; silver: light grey; nitrogen: blue; carbon: grey; hydrogen: white. Halogen atoms involved in the coordination to silver are shown as spheres.

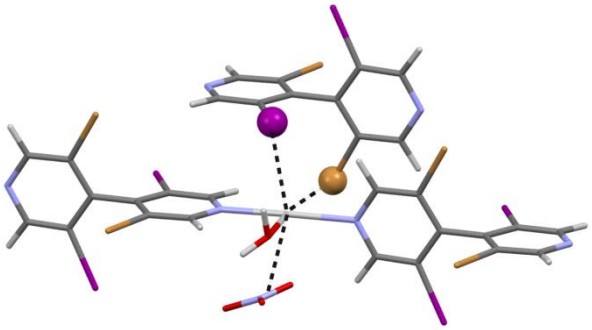
(i)



(ii)



(iii)



(iv)

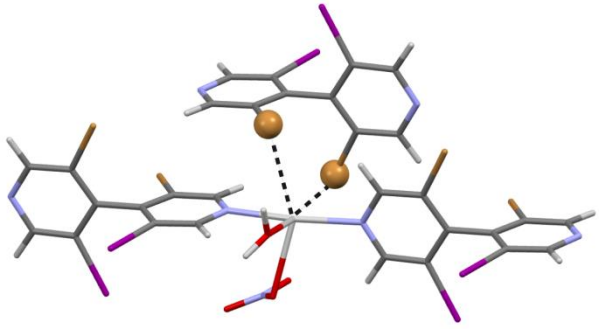
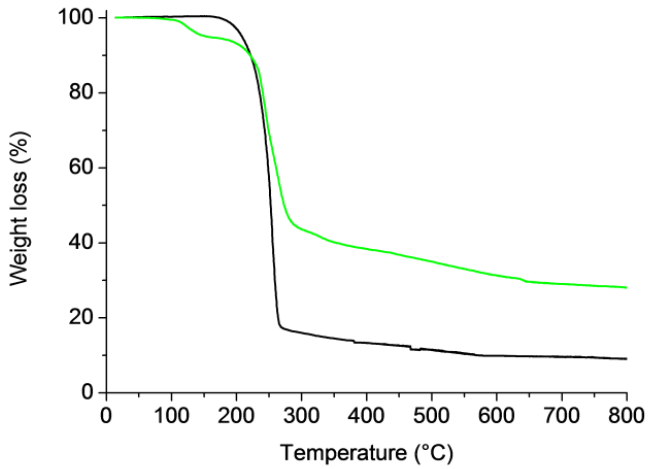


Fig. S5. (a) TGA weight loss of **C5a** (black) and **C5b** (green). (b) Main m/z corresponding to *i*PrOH recorded for **C5b** from MS analysis. Note: a Setaram Setsys Evolution 1750 Thermal Gravimetric Analyzer is coupled with a Pfeiffer GSD 301C Vacuum OmniStar mass spectrometer. Around 3 mg of the sample were placed in a platinum crucible and temperature was raised at a rate of 3°C/min from room temperature to 800 °C under a helium (Air Liquide Alphagaz 2, H_2O<) flux of 20 mL/min.

(a)



(b)

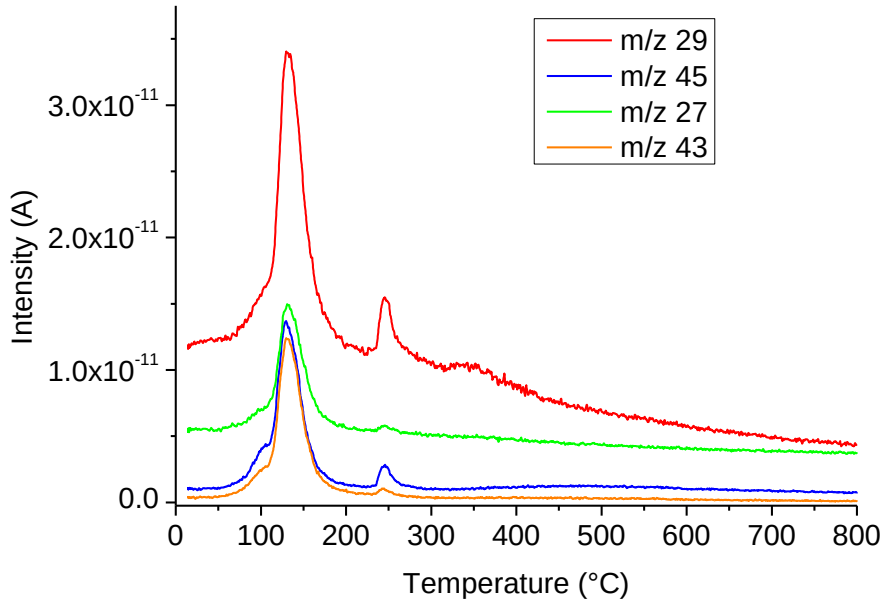
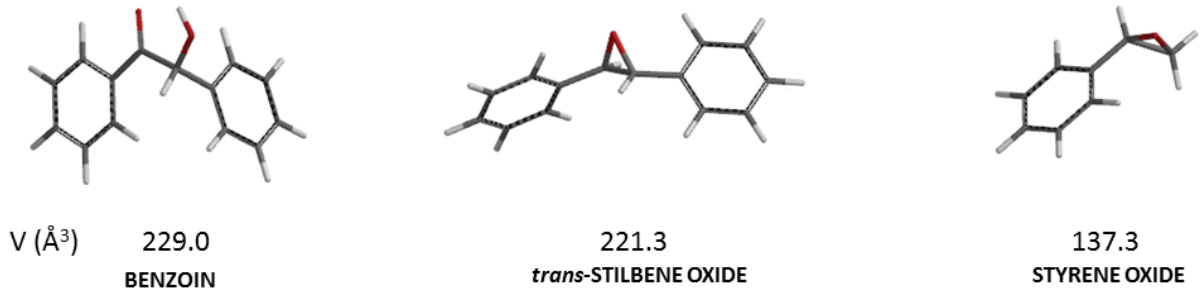


Fig. S6. (a) Small racemic compounds used for adsorption experiments. (b) Enantiomeric ratios detected by means of HPLC analysis (Lux Cellulose-2, *n*-hexane/2-propanol 90:10, *FR* 0.8 ml/min) of the solution of *rac*-styrene oxide (blue), the solutions of filtrate (red) and combined filtrate and extracts (green) after treatment on **C5b** for 5d at 25 °C ((*R*):(*S*) = 58:42).

a)



b)