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Supporting Information

Potassium iodide and bis(pyridylcarbamate) electrostatic synergy in the fixation reaction of CO_2 and epoxides

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1. Experimental section

1.1. Materials and Method

1.1.1 Materials

All starting chemicals and solvents were commercially available and were used without further purification. In this work, CO_2 was supplied by Handan Anke Factory with a purity of 99.99%.

1.1.2 Method

The reactions were carried out in a 100 mL stainless steel autoclave equipped with a magnetic stirrer and automatic temperature control system under atmospheric pressure by purging of CO_2. Pyridyl isocyanate was in situ generated by heating pyridyl acyl azide, which was obtained by treating the pyridyl acyl chloride with NaN_3.[1] Elemental analyses were done on a VarioEL instrument from Elementar analysen systeme GmbH. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Mercury plus-400 spectrometer using tetramethylsilane (TMS) as an internal standard in DMSO-d_6. Melting points were detected on an X-4 Digital Vision MP Instrument.

1.2. Synthesis of the bis(pyridylcarbamate).

The classic procedure of L^1 was synthesized as follow: 1.58 g (10.68 mmol) of 4-Pyridyl acyl azide in freshly dried 100 mL of toluene was refluxed under a nitrogen atmosphere for 2 h to give a pale yellow solution. Then 0.30mL (5.34 mmol) of ethylene glycol was added in solution and the mixture was refluxed for 0.5 h and then cooled to room temperature. A white powder was collected and washed with toluene, diethyl ether and dried in vacuum. Other products were obtained by a similar method as white powder.

1.3. Typical procedure for the carboxylation of epoxides

Propylene oxide (PO, 50mmol) was added into a 100 mL stainless steel autoclave equipped with a magnetic stirrer and automatic temperature control system. The desired amounts of catalysts of bis (pyridylcarbamate) and KI were introduced into the autoclave. After that the sealed container was charged with CO_2 at an appropriate pressure, then the reaction was started at a predetermined temperature. At the end of the reaction, the container was removed, allowed to cool to room temperature and CO_2 unreacted was vented. The product was evaporated to dryness under reduced pressure or recrystallization from ethanol to give the product.

2. The data of *L*^{1}–*L*^{5}

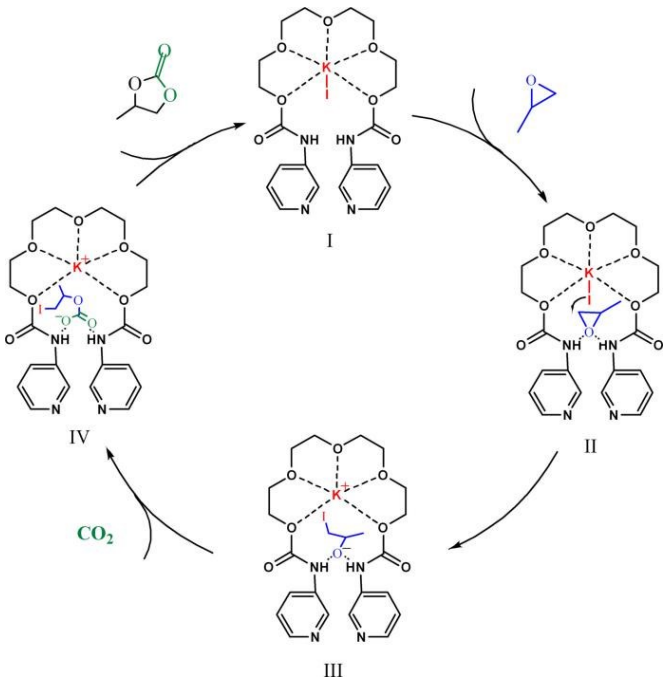
Ligand *L*^{1}, yield: 1.42 g (88%). M.p.:191–192°C. ^{1}H NMR (DMSO-d_6, 400 MHz): 4.39 (s, 4H,CH2); 7.43 (d, 4H, J = 5.0 Hz ,Py-H3); 8.37 (d, 4H, J = 5.0 Hz, Py-H2), 10.22 (s, 2H, NH). ^{13}C NMR (DMSO-d_6, ppm): 153.1, 150.4, 146.0, 112.5, 63.1. Anal. Calcd for $C_{14}H_{14}N_4O_4$ (302.3): C, 55.63; H, 4.67; N, 18.53; Found: C, 55.71; H, 4.51; N, 18.35.

Ligand *L*^{2}, yield: 93%. M.p.:210–211°C. ^{1}H NMR (DMSO-d_6, 400 MHz): 3.70 (s, 4H,CH5); 4.25 (s, 4H,CH4); 7.43 (d, 4H, J = 4.6 Hz, Py-H3), 8.36 (d, 4H, J = 4.6 Hz, Py-H2), 10.23 (s, 2H, NH). ^{13}C NMR (DMSO-d_6, ppm): 153.6, 150.7, 146.5, 112.8, 68.9,64.4. Anal. Calcd for $C_{16}H_{18}N_4O_5$ (346.34): C, 55.49; H, 5.24; N, 16.18 %; Found: C, 55.35; H, 5.31; N, 16.20 %.

Ligand L^3, yield: 76.3%, M.p.: 237–238 °C. ^{1}H NMR (DMSO-d_6, 400 MHz, ppm): 3.59 (s, 4H, CH7); 3.66 (d, 4H, J = 4.6 Hz, CH6); 4.22 (t, 4H, J = 4.4 Hz, CH5); 7.41 (d, 4H, J_1 = 6.4 Hz, Py-H3); 8.36 (d, 4H, J = 6.3 Hz, Py-H2); 10.21 (s, 2H, NH). ^{13}C NMR (DMSO-d_6, ppm): δ = 64.5, 69.0, 70.2, 112.8, 146.5, 150.7, 153.6. Anal. Calcd for $C_{18}H_{22}N_4O_6$ (390.4): C, 55.38; H, 5.68; N, 14.35 %. Found: C, 55.29; H, 5.56; N, 14.11 %.

Ligand L^4, yield: 57.3%, M.p.: 166–167 °C. ^{1}H NMR (DMSO-d_6, 400 MHz, ppm): 3.53 (s, 8H, CH7,CH8); 3.64 (t, 4H, J = 4.4 Hz, CH6); 4.22 (t, 4H, J = 4.2 Hz, CH5); 7.43 (d, 4H, J_1 = 6.12 Hz, Py-H3); 8.36 (d, 2H, J =6.08Hz, Py-H2); 10.24 (s, 2H, NH). ^{13}C NMR (DMSO-d_6, ppm): δ = 64.5, 68.9, 70.2, 70.3, 112.7, 146.5, 150.7, 153.6. Anal. Calcd for $C_{20}H_{26}N_4O_7$ (434.4): C, 55.29; H, 6.03; N, 12.90 %. Found: C, 55.25; H, 5.91; N, 13.08 %.

Ligand L^5, yield: 54.2%, M.p.: 86–87 °C. ^{1}H NMR (DMSO-d_6, 400 MHz, ppm): 3.52 (s, 8H, CH_2); 3.62 (t, 4H, J = 4.4 Hz, CH_2); 4.19 (t, 4H, J = 4.4 Hz, CH_2); 7.28 (dd, 2H, J_1 = 4.8 Hz, J_2 = 8.0 Hz, Py-H5); 7.86 (d, 2H, J = 8.0 Hz, Py-H4); 8.17 (d, 2H, J = 4.4 Hz, Py-H6); 8.61 (s, 2H, Py-H2); 9.90 (s, 2H, NH). ^{13}C NMR (DMSO-d_6, ppm): δ = 63.8, 68.5, 69.67, 69.71, 123.5, 124.9, 135.8, 140.1, 143.4, 153.5. Anal. Calcd for $C_{20}H_{26}N_4O_7$ (434.4): C, 55.29; H, 6.03; N, 12.90 %. Found: C, 55.23; H, 5.86; N, 13.11 %



Scheme S1. Possible Mechanistic Pathway

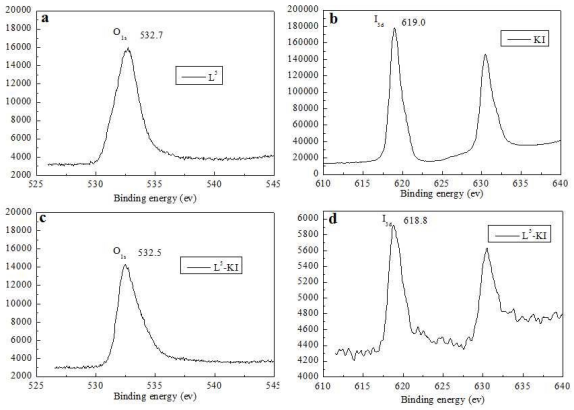


Fig. S1. Interaction of L^5 with KI identified by XPS

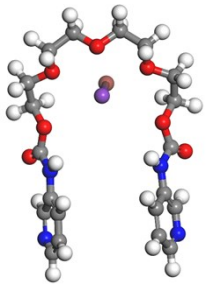


Fig. S2. Optimized structure of L^5 combined with KI

Notes and references

1 T. Werner and N. Tenhumberg, *J. CO_2 Util.*, 2014, **7**, 39.