

Supporting Information

Silver(I) supramolecular complexes generated from isophorone-based ligands: crystal structures and enhanced nonlinear optical properties through metal complexation

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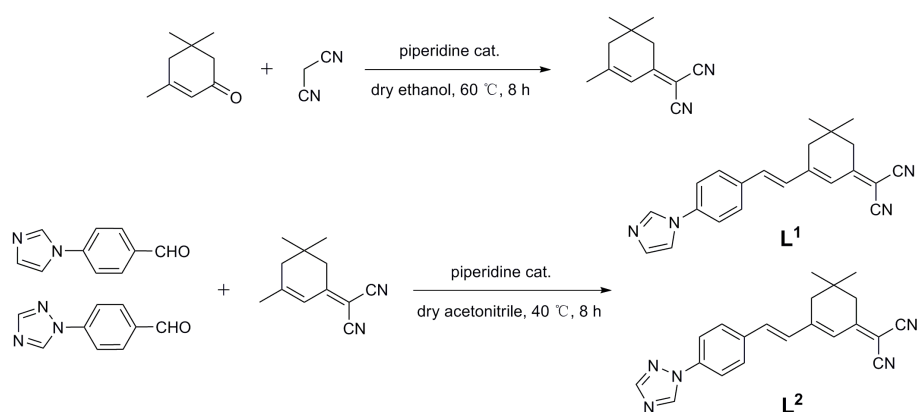
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Synthesis of L¹ and L²



Scheme S1 Synthesis of ligands L¹ and L².

Preparation of L¹. Under nitrogen, 4-(1H-imidazol-1-yl)benzaldehyde (2.4 g, 13.8mmol) and 2-(3,5,5-trimethylcyclohex-2-enylidene)malononitrile (2.6 g,

13.8mmol) were dissolved in dry acetonitrile (100 mL). 10 drops of piperidine was added and the solution was stirred at 40 °C for 8 h. After cooling the reaction mixture, the yellow precipitate was filtered, washed with acetonitrile, and dried. Yield: 2.50 g (53 %). ¹H NMR: (400 Hz, CD₃Cl), δ (ppm): 7.92 (s, 1H), 7.63 (d, *J* = 8.4 Hz, 2H), 7.44 (d, *J* = 8.4 Hz, 2H), 7.33 (s, 1H), 7.2 (s, 1H), 7.04 (d, *J* = 16.0 Hz, 1H), 7.02 (d, *J* = 16.0 Hz, 1H), 6.88 (s, 1H), 2.62 (s, 2H), 2.48 (s, 2H), 1.10 (s, 6H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) = 169.0, 153.1, 137.9, 135.4, 135.0, 134.8, 130.9, 130.0, 129.0, 124.1, 121.5, 117.8, 113.3, 112.6, 79.4, 43.0, 39.2, 32.0, 28.0. IR (KBr, cm⁻¹): 2965, 2925, 2870, 2218, 1608, 1572, 1511, 1455, 1400, 1054, 813. MALDI-TOF Calcd for C₂₂H₂₀N₄, 340.17; Found, 341.179.

Preparation of L². The yellow crystals L² was prepared according to a similar procedure of L¹ using 4-(1H-1,2,4-triazol-1-yl)benzaldehyde instead of 4-(1H-imidazol-1-yl) benzaldehyde. Yield: 4.00 g (85 %). ¹H NMR: (400 Hz, CD₃Cl), δ (ppm): 8.62 (s, 1H), 8.13 (s, 1H), 7.75 (d, *J* = 8.4 Hz, 2H), 7.66 (d, *J* = 8.8 Hz, 2H), 7.09 (d, *J* = 16.0 Hz, 1H), 7.04 (d, *J* = 16.0 Hz, 1H), 6.89 (s, 1H), 2.62 (s, 2H), 2.48 (s, 2H), 1.10 (s, 6H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) = 169.0, 153.0, 152.8, 140.7, 137.4, 135.5, 135.0, 130.2, 128.8, 124.3, 120.2, 113.2, 112.5, 79.5, 43.0, 39.2, 32.0, 28.0. IR (KBr, cm⁻¹): 2959, 2922, 2870, 2216, 1607, 1564, 1519, 1460, 1399, 1049, 811. MALDI-TOF Calcd for C₂₁H₁₉N₅, 341.16; Found, 342.171.

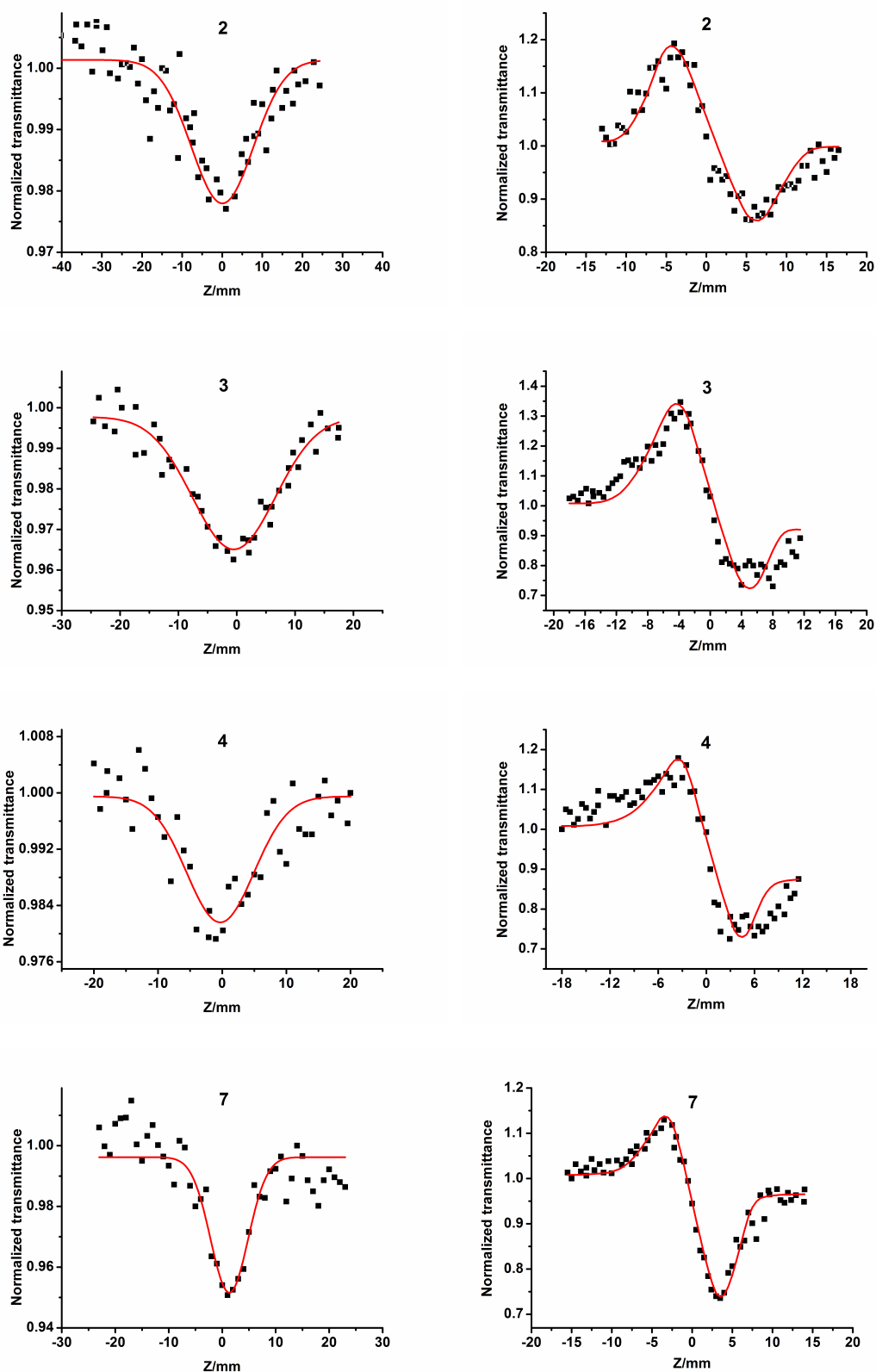


Fig. S1 The open aperture (right) and closed aperture (left) Z-scan data of complexes 2, 3, 4 and 7. The filled squares represent the experimental data and the solid curve is the theoretical data.