SUPPLEMENTARY DATA

Two Photon Absorption Properties of Four Coordinated Transition Metal Complexes of Tetraaryl-Azadipyrromethene Compounds

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1. SYNTHESIS

Synthesis of compound (L¹) (4.72 g, 16.65 mmol) 3-(4-methylphenyl)-4-nitro-1-phenylbutan-1one (2a) and ammonium acetate (45.00 g, 0.58 mol) were dissolved in ethanol (180 mL) and heated under reflux for 24 h. The reaction was cooled to room temperature, the solvent concentrated to 90 mL and filtered, and the isolated solid washed with ethanol (2 x 10 mL) to yield the product **3a** as a dark blue solid (1.75 g, 22%), mp 291-293 °C. ¹H NMR (CDCl₃, 500 MHz) δ : 8.02 (d, *J* = 8.5 Hz, 4H), 7.98 (d, *J* = 8.5 Hz, 4H), 7.57-7.47 (m, 6H), 7.28 (d, *J* = 8.5 Hz, 4H), 7.20 (s, 2H), 2.47 (s, 6H) (NH not observed). ¹³C NMR (CDCl₃, 101.6 MHz) δ : 155.0, 149.6, 142.7, 138.0, 132.3, 131.0, 130.0, 129.1, 129.0, 128.9, 126.5, 114.3, 21.4. IR (KBr disk) cm⁻¹: 1540. ES/MS calculated for 477,6 found [MH]⁺ : 478.9 Anal. Calcd for C₃₄H₂₇N₃: C, 85.50; H, 5.70; N, 8.80. Found: C, 85.31; H, 5.59; N, 8.83.

Synthesis of compound (L^2) L^2 was synthesized according to method given in the literature (1).

Synthesis of compound (L³) (2.42 g, 11.1 mmol) 3-(1- naphthylphenyl)-4-nitro-1-phenylbutan-1-one **(2a)** and ammonium acetate (30.0 g, 0.39 mol) were dissolved in ethanol (120 mL) and heated under reflux for 24 h. The reaction was cooled to room temperature, the solvent concentrated to 90 mL and filtered, and the isolated solid washed with ethanol (2 x 10 mL) to yield the product **3a** as a dark blue solid (0,732 g, 24%), mp 281-283 °C. ¹H NMR (CDCl₃, 400 MHz) δ : 8.28-8.26 (m, 2H), 7.98 (d, *J* = 6.8 Hz, 4H), 7.82-7.80 (m, 2H), 7.70 (d, *J* = 8.0 Hz, 2H), 7.60-7.57 (m, 4H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.48-7.43 (m, 6H), 7.24-7.21 (m, 2H) 7.20 (s, 2H), (NH not observed). ¹³C NMR (CDCl₃, 100 MHz) δ : 155.2, 150.6, 142.7, 134.0, 132.5, 132.1, 131.4, 130.3, 129.9, 129.4, 128.5, 128.3, 126.8, 126.5, 126.1, 125.6,125.3, 119.1. IR (KBr disk) cm⁻¹: 1530. ES/MS calculated for 549.67 found [MH]⁺ : 550.3 Anal. Calcd for C₄₀H₂₉N₃: C, 87.02; H, 5.30; N, 7.62. Found: C, 86.88; H, 5.26; N, 7.69

Synthesis of Complexes

Co(L¹)₂ : **[3-(4-methylphenyl)-5-phenyl)-1H-pyrrol-2-yl)]-[(3-(4-methylphenyl)-5-phenylpyrrol-2-ylidene)]amine (L¹)** (0.21 g, 0.44 mmol), CoCl₂.6H₂O (0.13 g, 0.55 mmol) and ammonium acetate (0.21 g, 2.70 mmol) in 15 ml n-butanol was stirred for 1 h at reflux. The mixture cooled to room temperature, the precipitate filtered as a dark blue powder. Flash column chromatography was performed over silica gel (hexane/CHCl₃ 1:2 v/v) to yield the desired product. (0.25 g, %75) mp >300 °C (decomposition). UV-vis (THF) max/nm: 610. ¹HNMR (400 MHz, CDCl₃) δ 63.90 (m, 4H), 15.97 (s, 8H), 14.31-14.15 (m, 16H), 8.84 (s, 4H), 6.28 (s, 4H), 2.44 (s, 4H), 1.53 (s, 12H); IR (KBr disc) *n*/cm-1: 1517, 2902. TOF HRMS ESI: Calcd ([C₆₈H₅₂N₆Co]) [MH⁺]: m/z = 1012.36637; found, m/z = 1012.36326.

Ni(L¹)₂ [3-(4-methylphenyl)-5-phenyl)-1H-pyrrol-2-yl)]-[(3-(4-methylphenyl)-5-phenylpyrrol-2-ylidene)]amine (L¹) (0.32 g, 0.67 mmol) and Ni(OAc)₂ (0.16 g, 0.90 mmol) in 15 ml nbutanol was stirred for 1 h at reflux. The mixture cooled to room temperature, the precipitate filtered as a dark blue powder. Flash column chromatography was performed over silica gel (hexane/CHCl₃ 1:2 v/v) to yield the desired product. (0.27 g, %78) mp >300 °C (decomposition) ¹H NMR (CDCl₃, 400 MHz) δ : 62.90 (s, 4H), 35.48 (s, 8H), 8.66 (s, 8H), 7.24 (s, 4H), 7.14 (d, *J* = 6.8 Hz, 8H), 1.54 (s, 12H), -1.74 (s, 8H); UV-vis (THF) *l*max/nm: 615. IR (KBr disc) *v*/cm⁻¹: 1261,1450,1511, 2902. TOF HRMS ESI: Calcd ([C₆₈H₅₂N₆Ni]) [MH⁺]: m/z = 1011.36852; found, m/z = 1011.36263. Cu(L¹)₂ : [3-(4-methylphenyl)-5-phenyl)-1H-pyrrol-2-yl)]-[(3-(4-methylphenyl)-5-phenylpyrrol-2-ylidene)]amine (L¹) (0.32 g, 0.67 mmol) and Cu(OAc)₂ (0.15 g, 0.82 mmol) in 15 ml n-butanol was stirred for 1 h at reflux. The mixture cooled to room temperature, the precipitate filtered as a dark blue powder. Flash column chromatography was performed over silica gel (hexane/CHCl₃ 1:2 v/v) to yield the desired product. (0.25 g, %75) mp >300 °C (decomposition) UV-vis (THF) max/nm: 575, 650. IR (KBr disc) n/cm^{-1} : 1363, 1446, 1519, 2922. TOF HRMS ESI: Calcd ([C₆₈H₅₂N₆Cu]) [MH⁺]: m/z = 1016.36277; found, m/z = 1016.35965.

Zn(L¹)₂ : [3-(4-methylphenyl)-5-phenyl)-1H-pyrrol-2-yl)]-[(3-(4-methylphenyl)-5-phenylpyrrol-2-ylidene)]amine (L¹) (0.32 g, 0.67 mmol) and Zn(OAc)₂ (0.16 g, 0.87 mmol)) in 15 ml n-butanol was stirred for 1 h at reflux. The mixture cooled to room temperature, the precipitate filtered as a dark blue powder. Flash column chromatography was performed over silica gel (hexane/CHCl₃ 1:2 v/v) to yield the desired product. (0.25 g, %75) mp >300 °C (decomposition). UV-vis (THF) max/nm: 600. ¹HNMR (400 MHz, CDCl₃) δ 7.77 (d, *J*= 8.0 Hz, 8H), 7.47 (d, *J*= 8.0 Hz, 8H) 7.22 (d, *J*= 8.4 Hz, 8H), 7.07-7.03 (m, 12H), 6.65 (s, 4H), 2.47 (s, 12H); ¹³CNMR (400 MHz, CDCl₃) δ 160.54, 148.17, 145.43, 137.62, 133.58, 131.92, 129.82, 129.22, 129.00, 128.22, 127.03, 116.76, 21.71; IR (KBr disc) *n*/cm⁻¹: 1243,1521, 2915. TOF HRMS ESI: Calcd ([C₆₈H₅₂N₆Zn]) [MH⁺]: m/z = 1017.36232; found, m/z = 1017.36102.

Co(L²)₂ : [(3-(4-methoxyphenyl)-5phenyl)-1H-pyrrol-2-yl)]-[(3-(4-methoxyphenyl)-5-fenylpyrrol-2-ylidene)]amine amine (L²) (0.23 g, 0.44 mmol), CoCl₂.6H₂O (0.13 g, 0.55 mmol) and ammonium acetate (0.21 g, 2.70 mmol) in 15 ml n-butanol was stirred for 1 h at reflux. The mixture cooled to room temperature, the precipitate filtered as a dark blue powder. Flash column chromatography was performed over silica gel (hexane/CHCl₃ 1:2 v/v) to yield the desired product. (0,25 g, %70) mp >300 °C. UV-vis (THF) max/nm: 617. ¹H NMR (400 MHz, CDCl₃) δ 63.55 (s, 4H), 15.46 (s, 8H), 14.65 (s, 8H), 8.87 (s, 4H), 7.97-7.91 (m, 16H), 7.32-7.25 (m, 4H), 6.50(s, 4H), 1.63 (s, 4H); IR (KBr disc) *n*/cm⁻¹: 1517, 2925. TOF HRMS ESI: Calcd ([C₆₈H₅₂N₆CoO₄]) [MH⁺]: m/z = 1076.34605; found, m/z = 1076.34551.

 $Ni(L^2)_2$: [(3-(4-methoxyphenyl)-5-phenyl)-1H-pyrrol-2-yl)]-[(3-(4-methoxyphenyl)-5-fenylpyrrol-2-ylidene)]amine amine (L²) (0.34 g, 0.67 mmol) and Ni(OAc)₂ (0.16 g, 0.90 mmol)

in 15 ml n-butanol was stirred for 1 h at reflux. The mixture cooled to room temperature, the precipitate filtered as a dark blue powder. Flash column chromatography was performed over silica gel (hexane/CHCl₃ 1:2 v/v) to yield the desired product. (0.29 g, %80) mp > 300 °C (decomposition). UV-vis (THF) max/nm: 616. ¹H NMR (CDCl₃ ,400 MHz) δ : 61.43 (s, 4H), 35.08 (s, 8H), 8.63 (s, 8H), 6.51 (d, *J* = 7.2 Hz, 8H), 3.50 (s, 12H), 1.58 (d, *J* = 7.2 Hz, 8H), -1.72 (d, *J* = 7.6 Hz, 8H); IR (KBr disc) *n*/cm⁻¹: 1241,1447,1518, 2927. TOF HRMS ESI: Calcd ([C₆₈H₅₂N₆NiO₄]) [MH⁺]: m/z = 1075.34820; found, m/z = 1075.34889.

Cu(L²)₂ : [(3-(4-methoxyphenyl)-5phenyl)-1H-pyrrol-2-yl)]-[(3-(4-methoxyphenyl)-5fenylpyrrol-2-ylidene)]amine amine (L²) (0.34 g, 0.67 mmol) and Cu(OAc)₂ (0.15 g, 0,82 mmol) in 15 ml n-butanol was stirred for 1 h at reflux. The mixture cooled to room temperature, the precipitate filtered as a dark blue powder. Flash column chromatography was performed over silica gel (hexane/CHCl₃ 1:2 v/v) to yield the desired product. (0.25 g, %70) mp >300 °C (decomposition). UV-vis (THF) max/nm: 584, 646.; IR (KBr disc) *n*/cm⁻¹: 1360, 1447, 1520, 2902. TOF HRMS ESI: Calcd ([C₆₈H₅₂N₆CuO₄]) [MH⁺]: m/z = 1080.34245; found, m/z = 1080.34048.

Zn(L²)₂ : [(3-(4-methoxyphenyl)-5phenyl)-1H-pyrrol-2-yl)]-[(3-(4-methoxyphenyl)-5fenylpyrrol-2-ylidene)]amine amine (L²) (0.32 g, 0.67 mmol) and Zn(OAc)₂ (0.16 g, 0,87 mmol)) in 15 ml n-butanol was stirred for 1 h at reflux. The mixture cooled to room temperature, the precipitate filtered as a dark blue powder. Flash column chromatography was performed over silica gel (hexane/CHCl₃ 1:2 v/v) to yield the desired product. (0.28 g, %78) mp > 300°C (decomposition). UV-vis (THF) max/nm: 601. ¹H NMR (400 MHz, CDCl₃) δ 7.84 (d, *J*= 8.0 Hz, 8H), 7.48 (m, 8H) 7.08-7.06 (m, 12H), 6.97 (d, *J*= 8.8 Hz 8H), 6.62 (s, 4H), 3.92 (s, 12H); ¹³CNMR (400 MHz, CDCl₃) δ 235.0, 215.9, 159.65, 145.0, 131.2, 129.1, 128.2, 127.6. 127.0, 116.0, 113.8, 55.6; IR (KBr disc) *n*/cm⁻¹: 1246, 1530, 2901. TOF HRMS ESI: Calcd ([C₆₈H₅₂N₆ZnO₄]) [MH⁺]: m/z = 1081.34200; found, m/z = 1081.33899.

Co(L³)₂ : [(3-(1-naphthyl)-5-phenyl)-1H-pyrrol-2-yl)]-[(3-(1-naphthyl-5-phenylpyrrol-2ylidene)]amine (L³) (0.23 g, 0.44 mmol), CoCl₂.6H₂O (0.13 g, 0.55 mmol) and ammonium acetate (0.21 g, 2.70 mmol) in 15 mL n-butanol was stirred for 1 h at reflux. The mixture cooled to room temperature, the precipitate filtered as a dark blue powder. Flash column chromatography was performed over silica gel (hexane/CHCl₃ 1:2 v/v) to yield the desired product. (0.25 g, %70) mp > 300 °C (decomposition). UV-vis (THF) max/nm: 595. ¹H NMR (400 MHz, CDCl₃) δ 65.03 (s, 4H), 17.20 (s, 8H), 16.07 (s, 4H), 10.52 (s, 4H), 10.35 (s, 8H), 9.06 (s, 4H), 8.23 (s, 4H), 6.56 (s, 4H), 5.91 (s, 4H), 1.65-0.93 (m, 4H); -14.21 (s, 4H); IR (KBr disc) n/cm^{-1} : 1522, 3040. TOF HRMS ESI: Calcd ([C₈₀H₅₂N₆Co]) [MH⁺]: m/z = 1156.36637; found, m/z = 1156.36231.

Ni(L³)₂ : [(3-(1-naphthyl)-5-phenyl)-1H-pyrrol-2-yl)]-[(3-(1-naphthyl-5-phenylpyrrol-2-ylidene)]amine (L³) (0.34 g, 0.67 mmol) and Ni(OAc)₂ (0.16 g, 0.90 mmol) in 15 mL n-butanol was stirred for 1 h at reflux. The mixture cooled to room temperature, the precipitate filtered as a dark blue powder. Flash column chromatography was performed over silica gel (hexane/CHCl₃ 1:2 v/v) to yield the desired product. (0.29 g, %80) mp > 300 °C (decomposition). UV-vis (THF) max/nm: 605. ¹H NMR (CDCl₃ ,400 MHz) δ : 62.33 (s, 4H), 35.46 (s, 8H), 9.12 (s, 8H), 7.34-7.30 (m, 8H), 6.59 (m, 4H), 6.45 (d, *J* = 8.0 Hz, 4H), 6.09-6.08 (m, 4H), 6.01 (d, *J* = 8.0 Hz, 4H), -4.43(s, 8H). IR (KBr disc) *n*/cm⁻¹: 1242, 1451, 1522, 3040. TOF HRMS ESI: Calcd ([C₈₀H₅₂N₆Ni]) [MH⁺]: m/z = 1155.36852; found, m/z = 1155.36532.

Cu(L³)₂ : [(3-(1-naphthyl)-5-phenyl)-1H-pyrrol-2-yl)]-[(3-(1-naphthyl-5-phenylpyrrol-2ylidene)]amine (L³) (0.34 g, 0.67 mmol) and Cu(OAc)₂ (0.15 g, 0,83 mmol) in 15 mL n-butanol was stirred for 1 h at reflux. The mixture cooled to room temperature, the precipitate filtered as a dark blue powder. Flash column chromatography was performed over silica gel (hexane/CHCl₃ 1:2 v/v) to yield the desired product. (0.25 g, %70) mp > 300 °C (decomposition). UV-vis (THF) max/nm: 573, 637. IR (KBr disc) *n*/cm-1: 1360, 1447, 1520, 3024. TOF HRMS ESI: Calcd ([C₈₀H₅₂N₆Cu]) [MH⁺]: m/z = 1160.36277; found, m/z = 1160.35761

Zn(L³)₂ : [(3-(1-naphthyl)-5-phenyl)-1H-pyrrol-2-yl)]-[(3-(1-naphthyl-5-phenylpyrrol-2-ylidene)]amine (L³) (0.32 g, 0,67 mmol) and Zn(OAc)₂ (0.16 g, 0.87 mmol)) in 15 ml n-butanol was stirred for 1 h at reflux. The mixture cooled to room temperature, the precipitate filtered as a dark blue powder. Flash column chromatography was performed over silica gel (hexane/CHCl₃ 1:2 v/v) to yield the desired product. (0.28 g, %78) mp > 300 °C (decomposition). UV-vis (THF) max/nm: 592. ¹H NMR (CDCl₃, 400 MHz) δ : 8.29 (d, *J* = 9.6 Hz, 2H), 8.11 (d, *J* = 7.6 Hz, 4H), 8.02 (d, *J* = 6.8 Hz, 2H), 7.84 (d, *J* = 7.6 Hz, 6H), 7.75-7.68 (m, 12H), 7.62-7.44 (m, 16H), 7.28-7.20 (m, 6H), 6.82 (s, 4H); ¹³C NMR (DMSO, 100 MHz) δ : 160.9, 160.5, 148.8, 148.0, 145.0, 144.4, 133.7, 133.6, 131.7, 131.6, 130.5, 130.1, 129.2, 128.6, 128.1, 126.7, 126.2, 126.1, 125.4, 122.1. IR (KBr disc) *n*/cm-1: 1248, 1529, 3053. TOF HRMS ESI: Calcd ([C₈₀H₅₂N₆Zn]) [MH⁺]: m/z = 1161.36232; found, m/z = 1161.35802.



Figure S1. ¹H NMR spectra of the compound $Ni(L^1)_2$ in CD_3Cl



Figure S2. ¹H NMR spectra of the compound $Ni(L^2)_2$ in CD_3Cl



Figure S3. ¹H NMR spectra of the compound $Ni(L^3)_2$ in CD_3Cl



Figure S4. High resolution mass spectra HRMS of the synthesized $Co(L^1)_2$ complexes.



Figure S5 High resolution mass spectra HRMS of the synthesized $Ni(L^1)_2$ complexes.



Figure S6. High resolution mass spectra HRMS of the synthesized $Cu(L^1)_2$ complexes.



Figure S7. High resolution mass spectra HRMS of the synthesized $Zn(L^1)_2$ complexes.







Figure S9. High resolution mass spectra HRMS of the synthesized $Ni(L^2)_2$ complexes.



Figure S10. High resolution mass spectra HRMS of the synthesized $Cu(L^2)_2$ complexes.



Figure S11. High resolution mass spectra HRMS of the synthesized $Zn(L^2)_2$ complexes.



Figure S12. High resolution mass spectra HRMS of the synthesized $Co(L^3)_2$ complexes.



Figure S13. High resolution mass spectra HRMS of the synthesized $Ni(L^3)_2$ complexes.



Figure S14. High resolution mass spectra HRMS of the synthesized $Cu(L^3)_2$ complexes.



Figure S15. High resolution mass spectra HRMS of the synthesized $Zn(L^3)_2$ complexes.



Figure S16Transient absorption spectra of ligand containing 4-Methoxyphenyl substituent (L^2) with 601 nm pump wavelength at different time intervals



Figure S17 Transient absorption spectra of metal complexes containing 4-Methylphenyl (L¹) substituents at different time intervals



Figure S18 Transient absorption spectra of metal complexes containing 1-Napthyl (L³) group at different time intervals

Notes and references

1 A. Gorman, J. Killoran, C. O'Shea, Tony Kenna, W. M. Gallagher, and D. F. O'Shea, *J. Am. Chem. Soc.* 2004, **126**, 10619.