Electronic Supplementary Material (ESI) for New Journal of Chemistry.

New highly fluorescent silver complexes and their thin materials obtained in spin coating method

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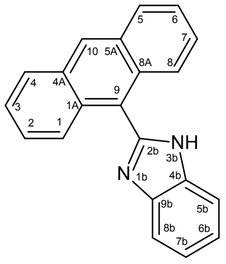
Electronic Supplementary Material (ESI)

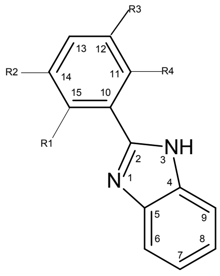
Synthesis of ligand epy(5-Brthca) L1

2(2-pirydyl)ethylamine 1 ml (8.36 mmol) was added dropwise to 0.994 ml (8.36 mmol) 5-bromo-2-thiophenecarboxaldehyde in 15 ml EtOH and stirring under reflux for 3 hours, after solvent evaporation oily product was obtained.

^1H NMR (400 MHz, $CDCl_3$) δ 8.50 (d, *J* = 7.7 Hz, 1H), 7.98 (m, 2H), 7.74 (m, 2H), 3.95 (t, *J* = 7.2 Hz, 2H), 3.16 (t, *J* = 7.2 Hz, 2H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 159.6 C1, 154.1 C9, 149.3 C4b, 144.0 C10, 136.3 C8A, 130.3 C10, 123.8 C4,5, 121.3 C1, 116.6 C13, 60.6 $C8H_2$, 39.4 $C7H_2$ (Figure 3) IR KBr 2928 ν($C-H_{Ar}$), 2851 ν CH_2, 1632 ν(C=N), 1473, 1432 ν (C=C), 1297ν(C-N) cm^{-1}.



L2



L3 R_3=OCH_3, R_2=Br, R_1=OH, R_4=H

L4 R_2= R_4= OCH_3, R_1= R_3 =H

Figure S1. Structural formula and atoms numbering scheme in 2-(anthracene-9-yl)-1H-benzo[d]imidazole **L2**, 2-(2H-benzimidazol-2-yl)-4-bromo-6-methoxyphenol **L3** and 2-(2,5-dimethoxyphenyl)-1H-benzimidazole **L4**

Ligand bzim-anthr L2

A solution of o-phenylenediamine (0.1500 g, 1.42 mmol) in 7 ml of ethanol was treated with solution of 9-anthracenecarboxaldehyde (0.5900 g, 2.84 mmol) in the same solvent and stirred at 78°C for 3 hours. The resulting orange filtrate was slowly evaporated to the dryness. The orange crystals were obtained from this ethanol solution. (Figure S1) Yield 0.2300 g (55%), t.m. 261°C.

^{1}H NMR [ppm] (400 MHz, DMSO-d$_6$) δ 13.0 (br, s, 1H, NH), 8.85 (s, 1H, H10), 8.22 (d, *J* = 8.4 Hz, 2H, H4,5), 7.83 (m, 1H, 5b), 7.68 (dd, *J* = 0.8 Hz, 2H, 1,8), 7.61 (m, 3H, 6,7,6b), 7.52 (m, 2H,7b,8b), 7.32 (m, 2H, H2,3), 3.33 (s, 1H). ^{13}C NMR [ppm] (400 MHz, DMSO-d$_6$) δ 149.9 C2b, 144.2 C9, 135.1 C4b, 9b, 131.1 C5A, 131.0 C4A, 129.3 C1A,8A, 128.9 C10, 127.3 C4,5, 126.3 C7, 126.1C6b, 126.0 C6, 123.0 C1,8, 122.0 2,3, 119.5 C5b, 111.8 C7b,8b. (Figure 2) FT-IR (KBr) 2936 C-H$_{Ar}$ 1667 (C=C), 1488 (C=N), 1464, 1334 (C=C), 1283, 1259 ν(C-N), 1178, 957, 944, 837, 750 cm^{-1}.[1]

2-(1*H*-benzimidazol-2-yl)-4-bromo-6-methoxyphenol L3

A solution of o-phenylenediamine (0.3000 g, 2.77 mmol) in 15 ml of ethanol was treated with solution of 5-bromo-2-hydroxy-3-methoxybenzaldehyde (1.2819 g, 5.54 mmol) in the same procedure as for **L1** (78°C for 16 hours). The orange crystals suitable for X-ray data collection were obtained from ethanol solution. Yield 97%. t.m. 245°C.

^{1}H NMR [ppm] (700 MHz, DMSO-d_6) δ 13.41 (s, 1H, NH), 13.29 (s, 1H, OH), 7.89 (d, *J*=1.2 Hz, 1H, H13), 7.73 (s, 1H, H6), 7.63 (s, 1H, H9), 7.31 (s, 2H, H7,8), 7.23 (d, *J*=2 Hz, 1H, H15), 3.86 (s, 3H-OCH_3); ^{13}C NMR [ppm] (700 MHz, DMSO-d_6) δ 151.04 C2, 150.14 (C12), 148.12 (C14), 140.97 C4,5 133.5 C5, 124.11 C7, 123.16 C8, 120.08 C13, 118.53 C6, 116.86 C15, 114.20 C11, 112.16 C9, 110.22 C10, 56.64 $O\underline{C}H_3$.[2] (Figure S1) FT-IR (KBr) 3097, 2942, 2843 (H-Ar) 1609 (C=C), 1564, 1462 (C=N), 1440, 1390, 1365, 1322, 1269 ν(C-N), 1250, 1220, 1200, 1187, 1110 (C-N), 970, 871, 771 cm^{-1}.

The **L4** ligand 2-(2,5-dimethoxyphenyl)-1*H*-benzimidazole was synthesized in the same procedure as **L3**.

^{1}H NMR [ppm] (400 MHz, $CDCl_3$) 10.89 (NH), 8.15 (t, J =1.2 Hz, 1H, H7, H6), 7.38 (s, 1H, H13), 7.28 (m, 2H)), 6.99 (m, 2H), 4.01 (s, 3H-OCH3), 3.88 (s, 3H-OCH3); 13C NMR [ppm] (400 MHz, CDCl3) δ 154.25 C2, 151.27 C(12), 149.83 C(14), 128.34 C(11), 122.60 C(10), 118.24 C(7), 118.24 C(6), 113.22 C(5), 113.01 C(8), 56.42 (OCH3), 56.00 (OCH3). (Figure S1) m.p. 215°C. Yield: 75%. ATR-IR 2949, 2937 ν(H-Ar), 1675 ν(C=C), 1610, 1587 (C=N), 1490, 1463, ν(C=C), 1273, 1261 ν(C-N), 1220, 1201, ν(C-N), 1040 cm^{-1}.

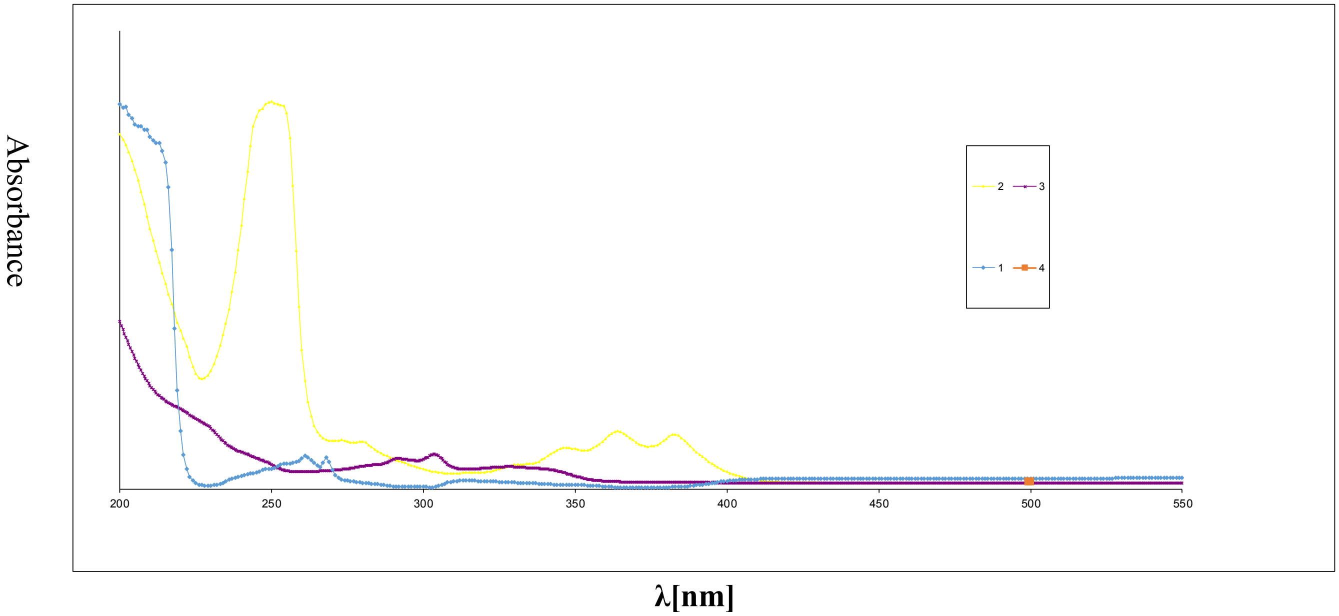


Figure S2 .UV-Vis absorption spectra of complexes in MeCN solution.

Determination of the fluorescence quantum yield

The quantum yield was calculated by using following equation:

$$\mathbf{\Phi_x = \Phi_{ST}\ x\ (}\frac{I}{I_R}\ \mathbf{x}\ \frac{OD_R}{OD}\ \mathbf{x}\ \frac{\eta^2}{\eta_R^2}\mathbf{)\ [1]}$$

Φ_x - fluorescence quantum yield

OD –fluorescence intensity

I absorption

η refractive index of solvent

R- reference fluorophore of known quantum yield here chinine

$\Phi_{ST} = 0.54$

$$\frac{\eta^2}{\eta_R^2} = \mathbf{1.021}$$

[1] M.W. Allen, Thermo Scientific, technical note 52019.

acetonitrile solution

2

$$\frac{OD_R}{OD} = 10171575/10110380 = 1.006$$

$$\frac{\eta^2}{\eta_R^2} = 0,271/0,28 = 0,967$$

$\Phi_{\mathbf{2}}$= 0.54x1.006x0.967x1,021=0.53

The other calculations of fluorescence yield of the rest of compounds was done in the same way.

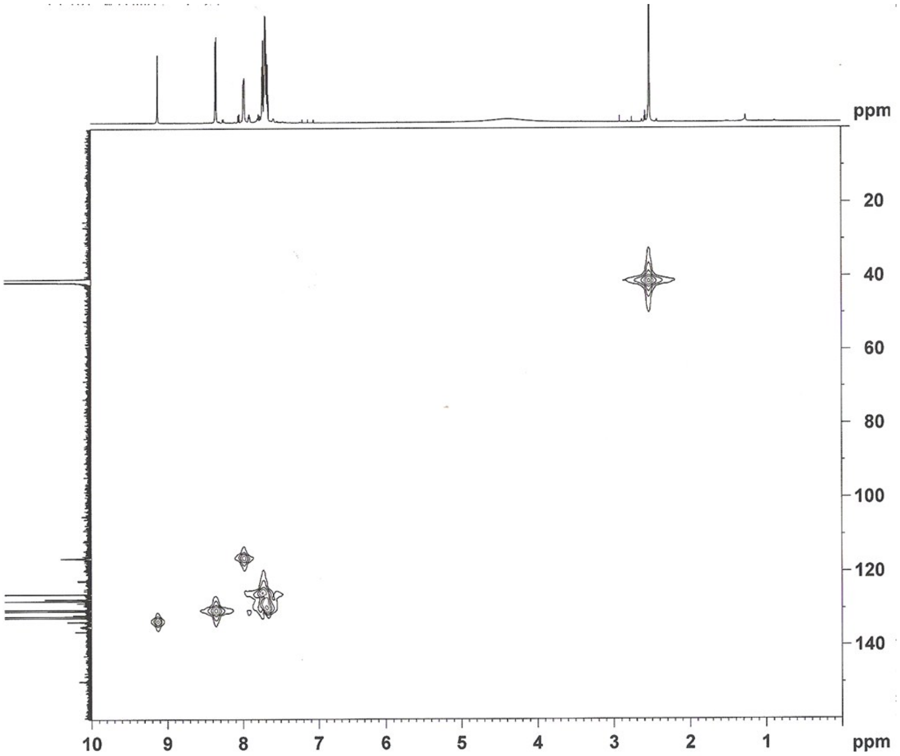


Figure S3. $^1H^{13}C$ NMR spectrum of **2** DMSO-d_6 700 MzH.

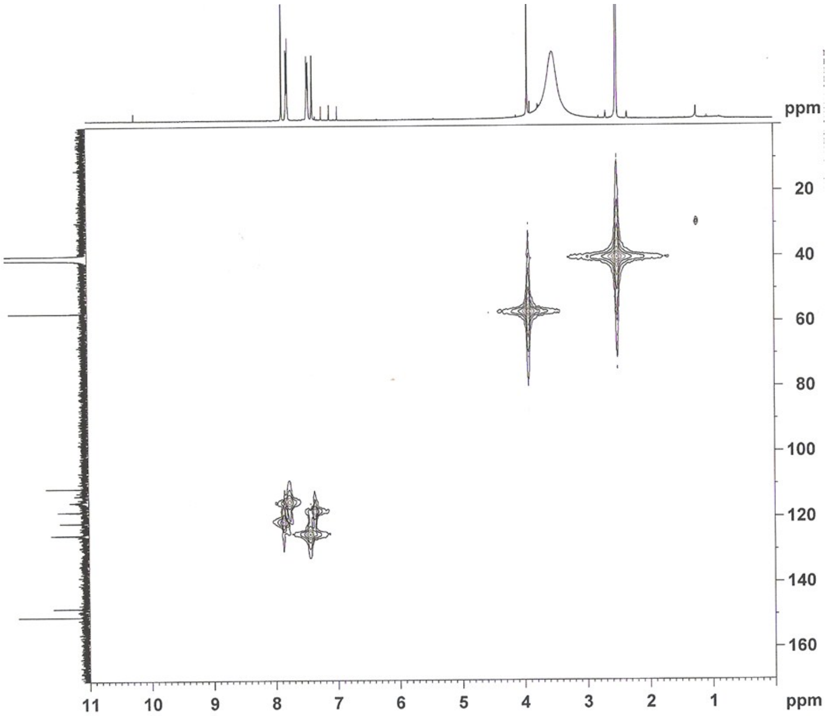


Figure S4. $^{1}H^{13}C$ NMR spectrum of **3** DMSO-d_6 700 MzH.

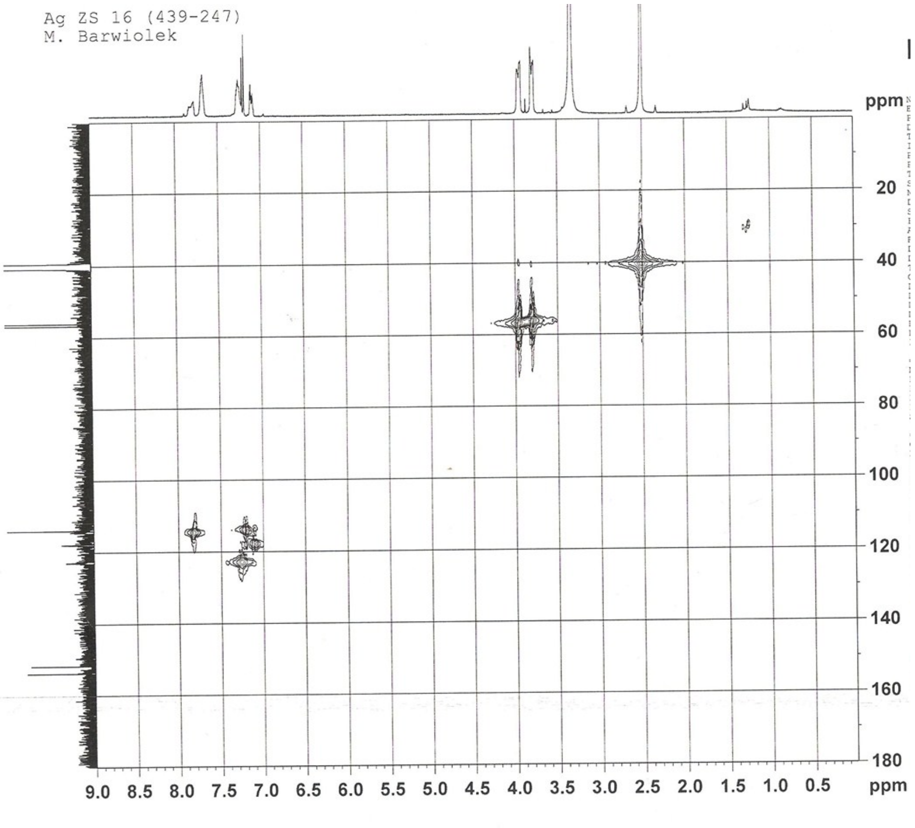


Figure S5. $^{1}H^{13}C$ NMR spectrum of **4** DMSO-d_6 700 MzH.

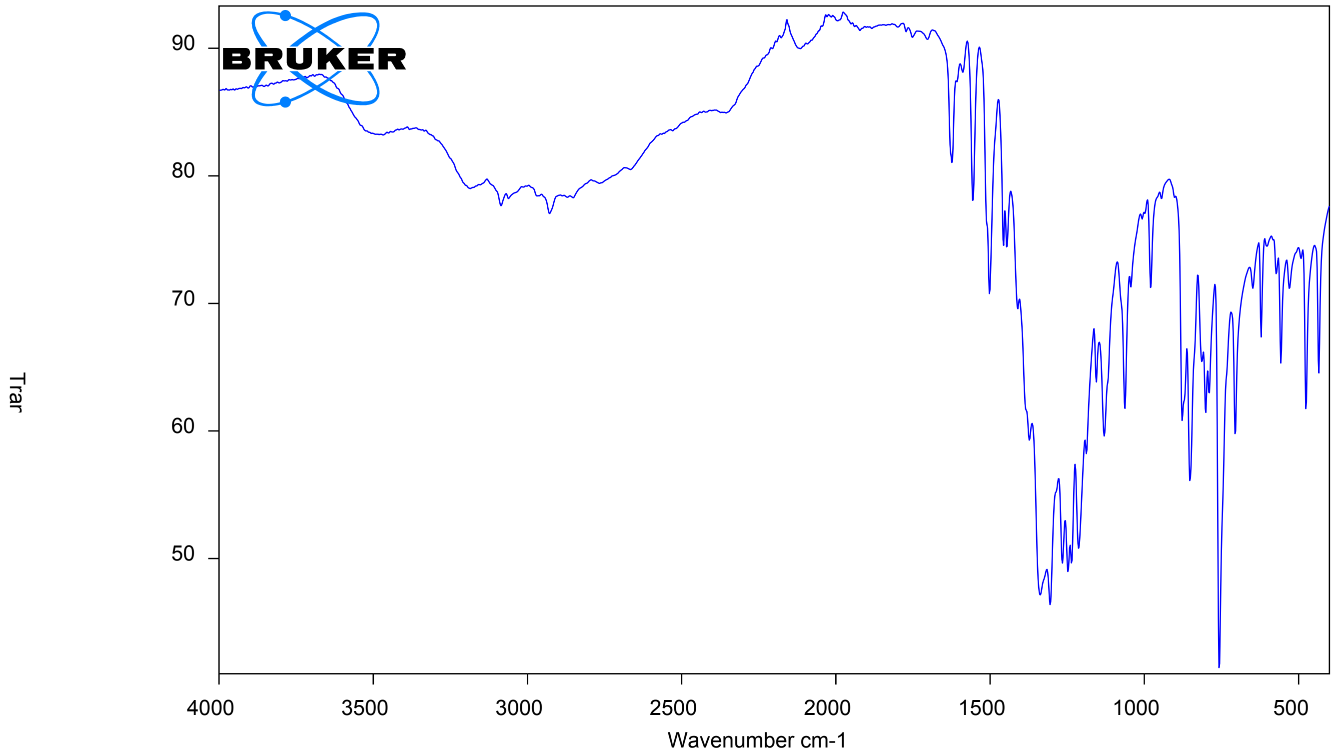


Figure S6. IR ATR spectrum of **3.**

height amplitude phase

Figure S7. AFM image of **2**, PMMA/Si(111) 2500 rpm 30s, 5000 rpm 20sx5.

R

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[1] D. Mahesh, P. Sadhu, T. Punniyamurthy, *J. Org. Chem.* 2015, **80**, 1644.

[2] X. Yang, R. A Jones, M. J. Wiester, M. M. Oye, W. K. Wong, *Crystal Growth & Design*, 2010, **10**, 970.