Electronic Supplementary Information

Self-assembly of singlet-emitting double-helical silver dimers: the curious coordination chemistry and fluorescence of bisquinolylpyridone.

Charlotte M. A. Farrow,[a] Geoffrey R. Akien,[a] Nathan R. Halcovitch,[a] James A. Platts*[b] and M. P. Coogan*[a]

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S1 Experimental Procedures and Data

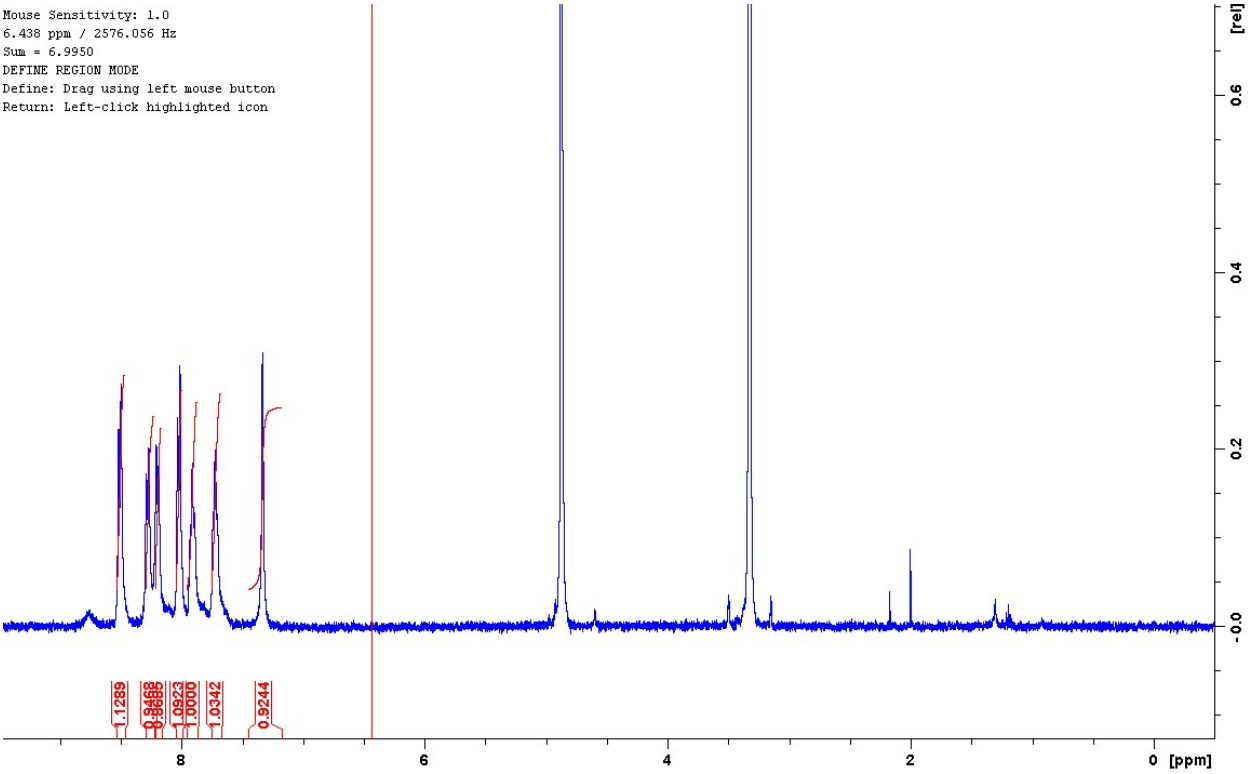
2,6-Bis(2-quinolyl)-4(1H)-pyridone 1.

To a stirred suspension of 1,5-bis(2-quinolyl)-pentane-1,3,5-trione (888 mg, 24.1 mmol) in methanol (25 ml) at 60° C was added ammonium acetate (1.50 g, 19.4 mmol) and the stirred mixture heated at 60 °C for 66 h. After cooling to room temperature, the reaction mixture was treated with water (100 ml) and a yellow gel-like substance separated by prolonged vacuum filtration. The product was recrystallised from an ethanol acetone mixture to give the title compound as a white solid (595 mg, 1.77 mmol, 74%). ^{1}H NMR (400 MHz, CD_3OD): δ 8.51 (2H d, J= 8.1 Hz, H8,8') 8.28 (2H, d, J=8.2 Hz, H4,4') 8.20 (2H, d, J = 8.2 Hz, H3,3') 8.03 (2H, d, J=8.2 Hz, H5,5') 7.91 (2H, m, H6,6') 7.72 (2H, m, H7,7') 7.33 (2H, s, pyridone H3,3'). ^{13}C{^{1}H} NMR (400 MHz, DMSO-d_6): δ 166.6, 156.7, 155.6, 147.6, 137.5, 130.5, 129.7, 128.6, 128.4, 127.6, 119.3, 109.8 IR ν max: 3271, 3055, 1634 (C=O), 1564 1502, 1429, 1258 cm^{-1}. m/z (ESI, HRMS 350.1277, $C_{23}H_{15}N_3O$ predicts 350.1288. $C_{23}H_{15}N_3O.2H_2O$ requires C 71.7 H 4.97 N 10.9 found C 71.7 H 4.67 N 11.1 %

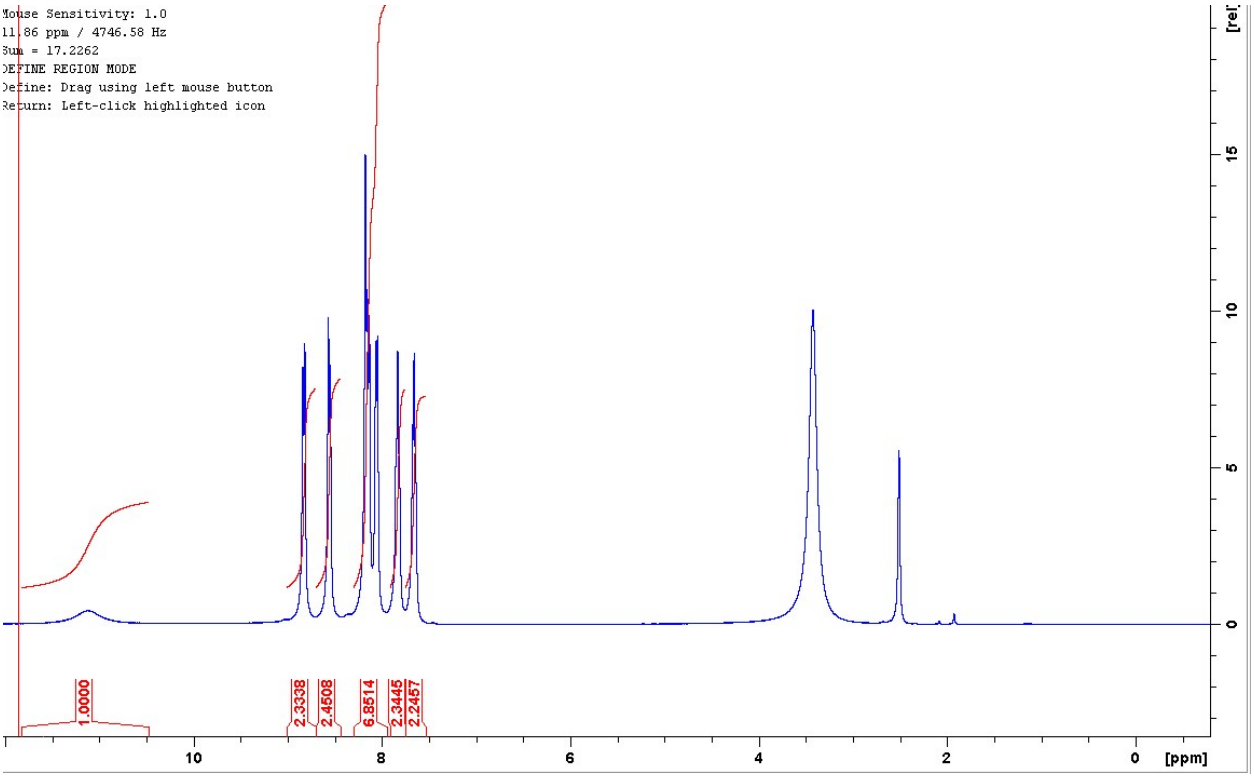
Di-(silver-(I)-(2,6-Bis(2-quinolyl)-4(1H)-pyridonyl)) tetrafluoroborate 2.

To a round bottom flask was added ligand **1** (67.0 mg, 0.191 mmol) and silver (I) tetrafluoroborate (40 mg, 0.206 mg) and acetonitrile (20 ml) and the mixture heated at reflux for 5 minutes during which time the reactants passed into solution. The mixture was then concentrated under vacuum to 2 ml and treated with diethyl ether (2 ml) giving a white precipitate of the title compound (68 mg, 0.128 mmol, 67%). ^{1}H NMR (400 MHz, CD_3CN): δ 8.07 (1H, d, J=8.1 Hz, H8,8') 7.80 (1H, d, J= 7.7 Hz, H5,5') 7.63 (1H, s, pyridine H3,3') 7.58 (3H, m, H3,3',4,4',7,7') 7.49 (1H, m, H6,6'). ^{13}C{^{1}H} NMR (400 MHz, CD_3CN, saturated solution, some peaks not observed): δ 145.2, 139.0, 131.4, 129.1, 128.3, 128.2, 128.2, 120.3, 117.3, 113.0. m/z (ESI, HRMS) observed 805.1483 $C_{46}H_{30}N_6O_2Ag$ (L_2Ag) requires 805.1476. $C_{46}H_{30}N_6O_2Ag_2B_2F_8.H_2O$ requires C 50.0 H 2.92 N 7.60 found C 49.8 H 2.71 N 7.99 %

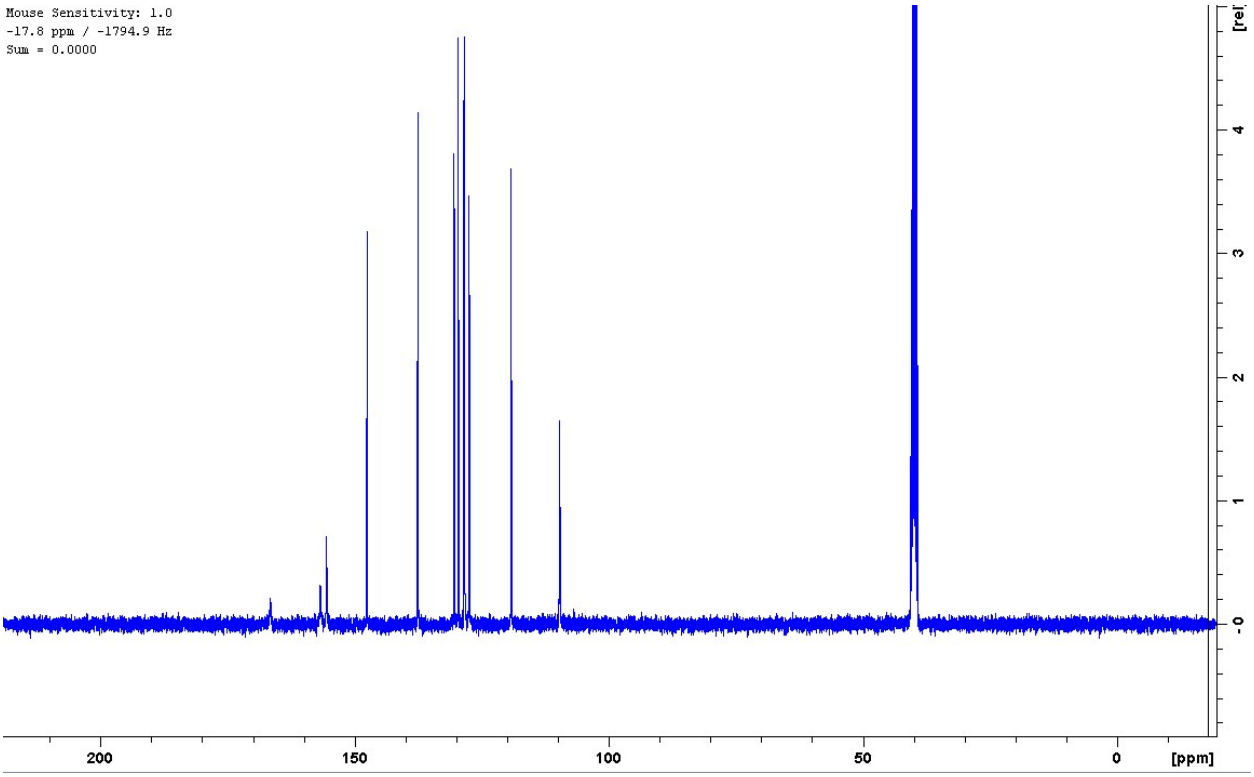
S2 Spectral Data



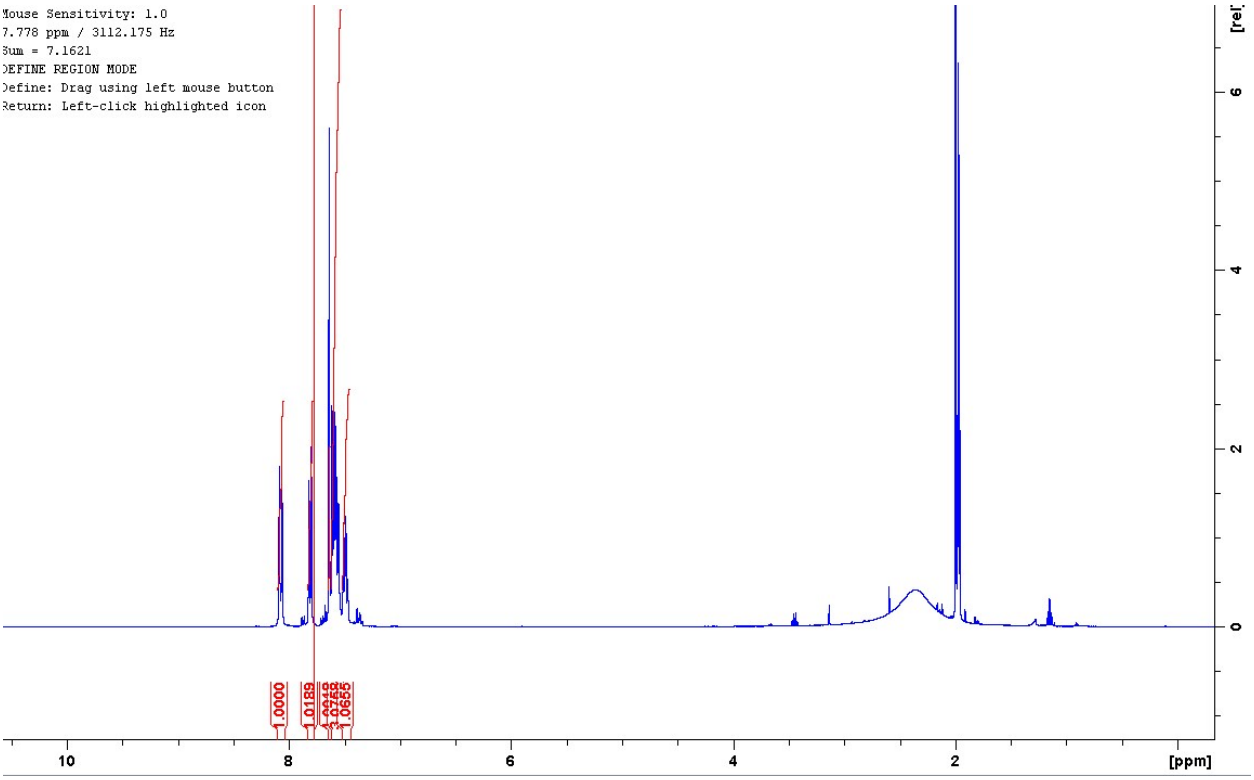
^{1}H NMR of 1 (MeOD-d_4)



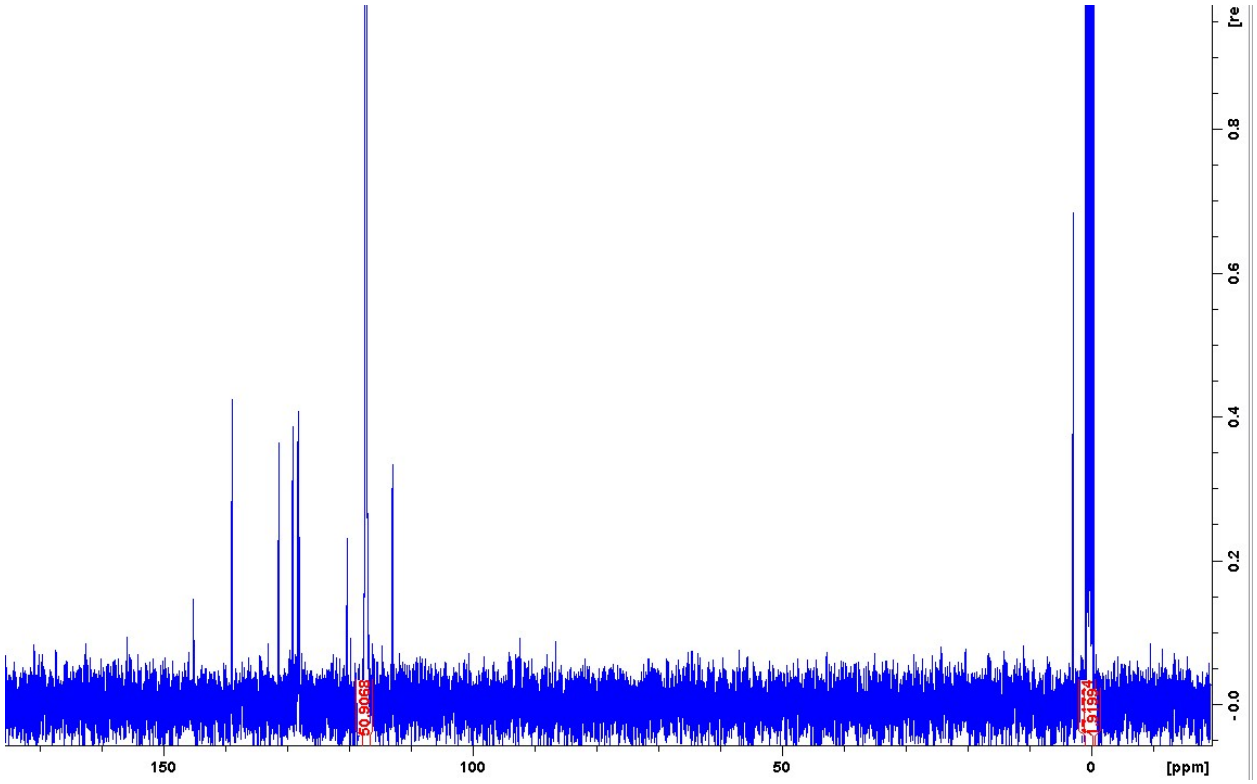
^{1}H NMR of 1 (DMSO-d_6)



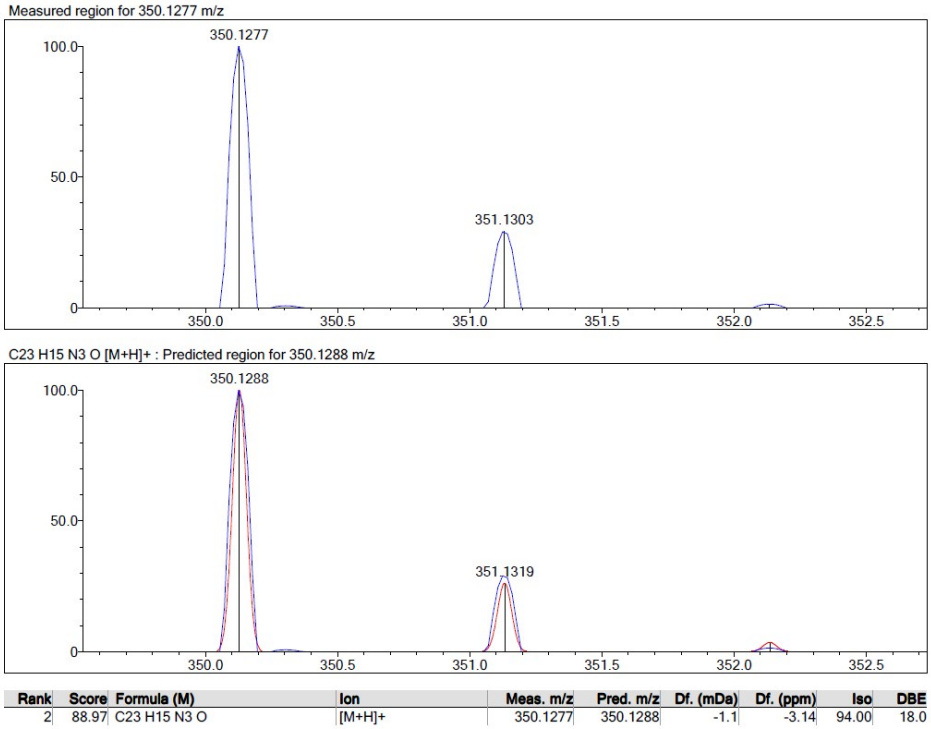
^{13}C NMR of 1 (DMSO-d_6)



^{1}H NMR of 2 (CD_3CN)

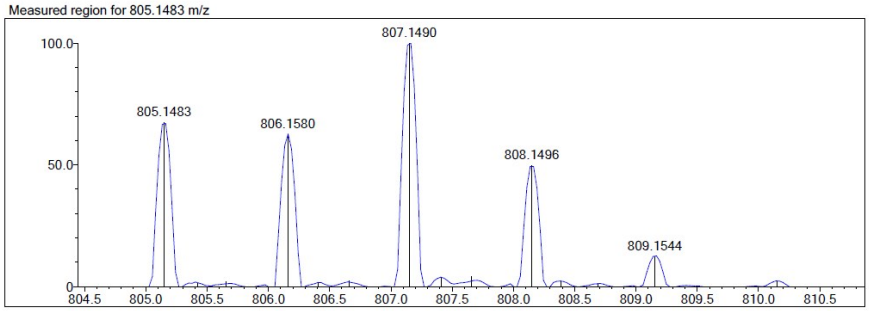


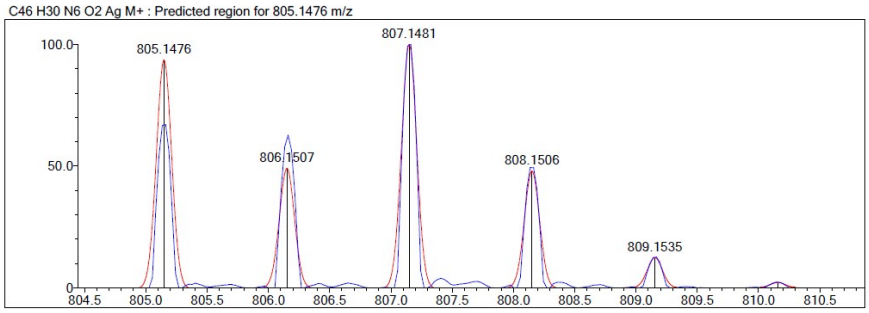
^{13}C NMR of 2 (CD_3CN)



Rank	Score	Formula (M)	Ion	Meas. m/z	Pred. m/z	Df. (mDa)	Df. (ppm)	Iso	DBE
2	88.97	C23 H15 N3 O	[M+H]+	350.1277	350.1288	-1.1	-3.14	94.00	18.0

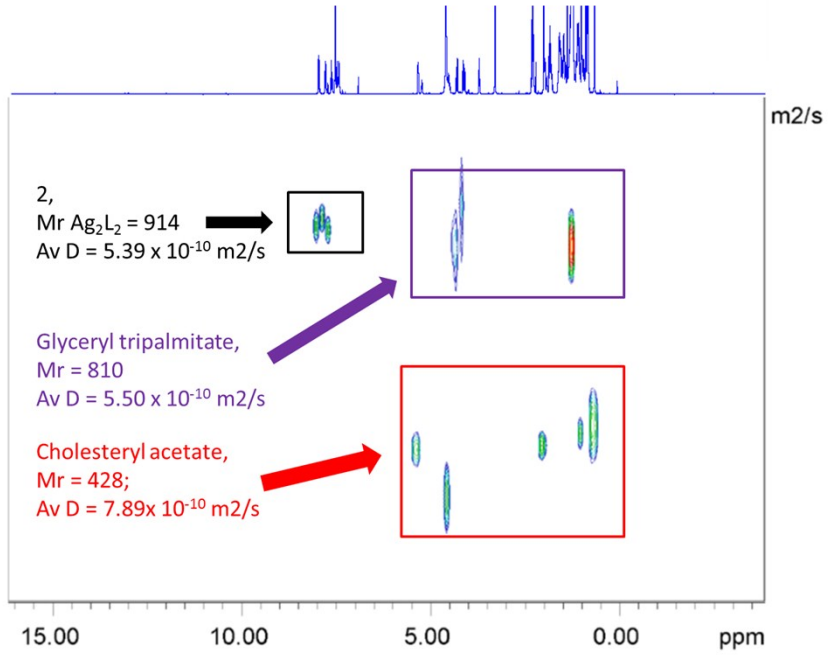
HMRS of 1 (ESI)





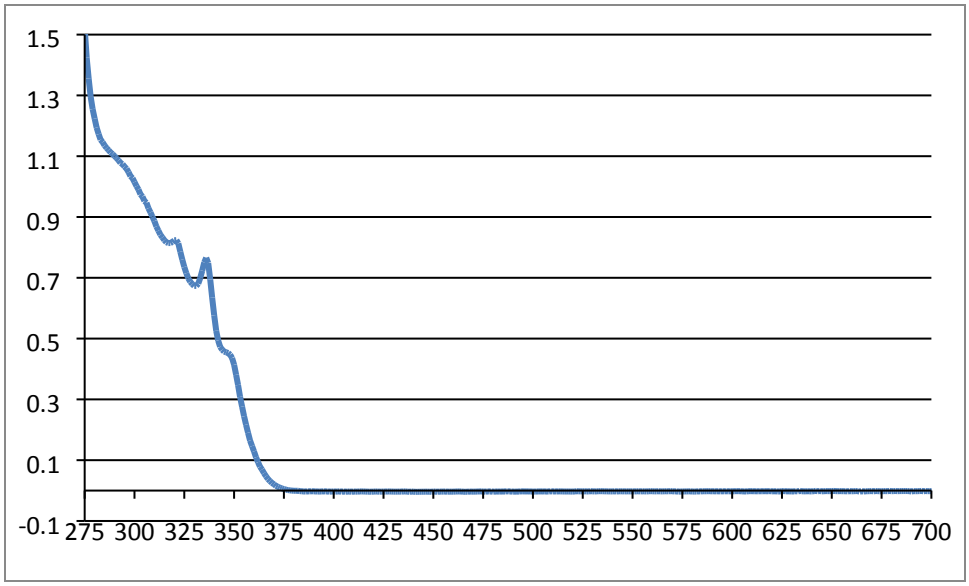
Rank	Score	Formula (M)	Ion	Meas. m/z	Pred. m/z	Df. (mDa)	Df. (ppm)	Iso	DBE
1	60.46	C46 H30 N6 O2 Ag	M+	805.1483	805.1476	0.7	0.87	60.46	34.5

HMRS of 2 (ESI)

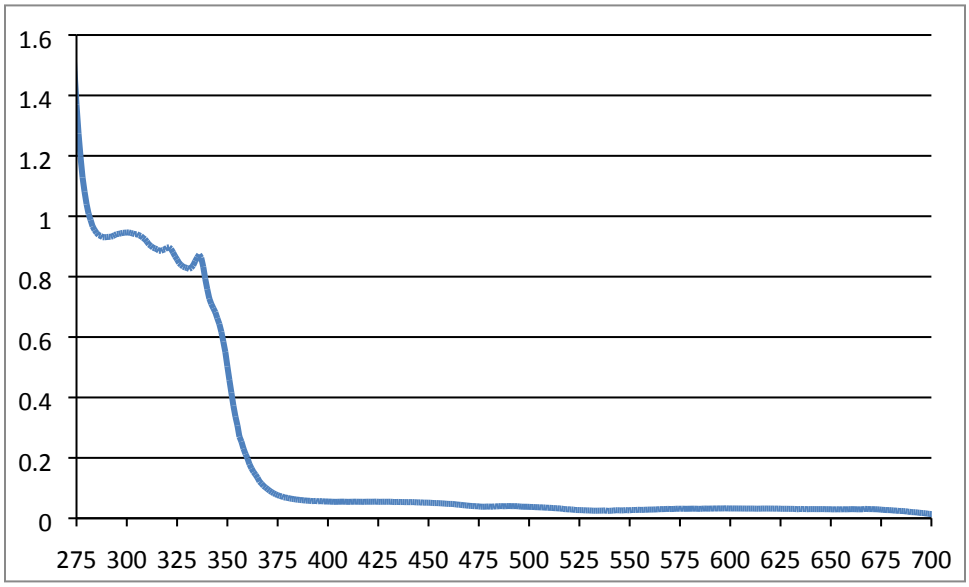


DOSY Spectrum of 2.

The insolubility of **2** in solvents for which DOSY/Mr relationships are accurately established prevented direct Mr assessment of **2** which was instead compared to internal standards, glyceryl tripalmitate and cholesterol acetate to assess solution speciation of **2** (c.f. monomeric forms AgL, Mr = 457, AgL2, Mr= 807).



UV Vis of **1** (0.003 mM MeCN).



UV Vis of **2** (0.015 mM MeCN).

S2 Computational Procedures and Results.

Theoretical Calculations

Geometry of **1** and **2** were fully optimised without any symmetry constraint using the M06-2X functional [a] and a basis set consisting of 6-31G(d) on light atoms [b] and Stuttgart-Dresden basis/ECP on Ag [c]. TD-DFT calculations were performed using the range-separated CAM-B3LYP method [d], with the same basis set. All such calculations used Gaussian09 [e]. ZINDO/S [f] calculations on DFT optimised geometries were carried out using the ORCA package [g].

[a] Y. Zhao and D. G. Truhlar, Theor. Chem. Acc., 2008, 120, 215.

[b] R. Ditchfield, W. J. Hehre, and J. A. Pople, J. Chem. Phys., 1971, 54, 724; P. C. Hariharan and J. A. Pople, Theor. Chem. Acc., 1973, 28, 213.

[c] D. Andrae, U. Haeussermann, M. Dolg, H. Stoll, and H. Preuss, Theor. Chem. Acc., 1990, 77, 123.

[d] T. Yanai, D. Tew, and N. Handy, Chem. Phys. Lett., 2004, 393, 51.

[e] Gaussian 09, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski,

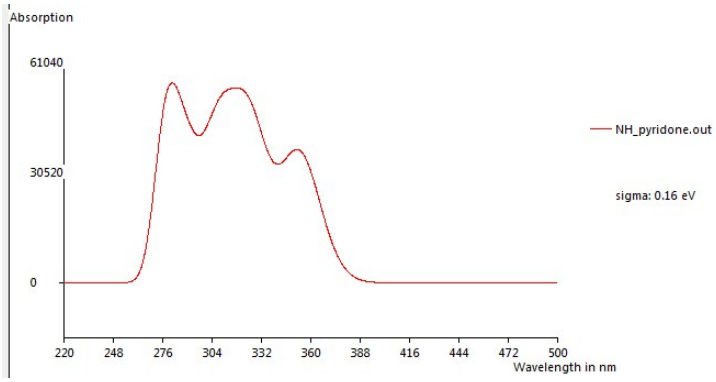
and D. J. Fox, Gaussian, Inc., Wallingford CT, 2010.

[f] F. Neese, Wiley interdisciplinary Reviews - Computational Molecular Science, 2012, 2, 73.

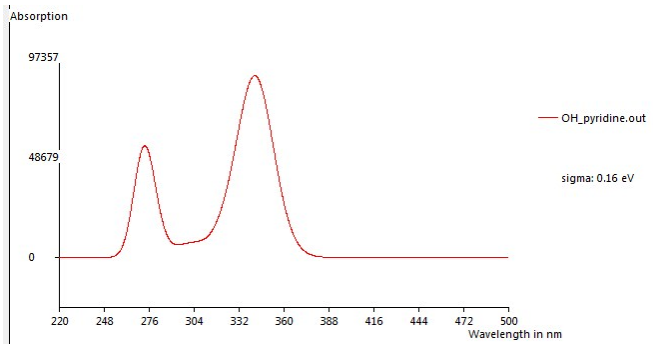
[g] M. C. Zerner, G. H. Lowe, R. F. Kirchner, and U. T. Mueller-Westerhoff, J. Am. Chem. Soc., 1980, 102, 589.

ZINDO orbital energies for 1.

STATE 1: E= 0.091797 au 2.498 eV 20147.2 cm**-1
59a -> 64a : 0.785075 (c= -0.88604482)
59a -> 67a : 0.011267 (c= -0.10614526)
59a -> 70a : 0.012985 (c= 0.11395308)
59a -> 71a : 0.080375 (c= 0.28350400)
59a -> 72a : 0.013697 (c= -0.11703354)
59a -> 73a : 0.018726 (c= 0.13684160)
59a -> 83a : 0.030726 (c= -0.17528945)



Predicted absorption spectrum for 1 (pyridone form)



Predicted absorption spectrum for 1 (hydroxypyridine form)

Pyridone

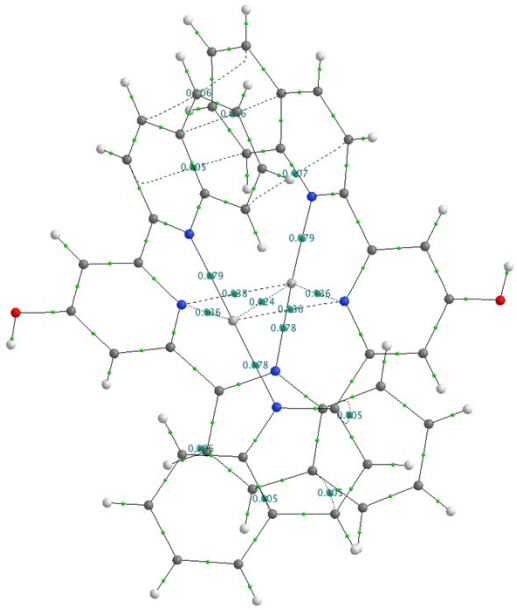
State	Energy (cm-1)	Wavelength (nm)	fosc
1	27473.8	364.0	0.001214229
2	28265.5	353.8	0.258966995
11	13718.5	728.9	spin forbidden (mult=3)

Pyridine

1	20147.2	496.3	0.001018456
2	29164.0	342.9	0.820051302
11	12841.0	778.8	spin forbidden (mult=3)

Table S 1

Predicted (ZINDO) Emission Bands 1 in each form.



Bond Paths for 2**.**

S4 Crystallographic Data

Crystallographic Tables for 1, 1-a, 1-b, 2, 2-a.

Identification code	**1**	**1-a**	**1-b**
CCDC number	1572595	1572597	1572598
Empirical formula	$C_{23}H_{15}N_3O_1$	$C_{46}H_{30}N_6O_2$	$C_{92}H_{60}N_{12}O_4$
Formula weight	349.38	698.76	1397.52
Temperature/K	100.00(10)	100.00(10)	100.01(10)
Crystal system	monoclinic	monoclinic	triclinic
Space group	I2/a	$P2_1/n$	P-1
a/Å	26.3237(5)	18.2068(4)	11.5071(2)
b/Å	3.84158(8)	6.07880(19)	17.7155(4)
c/Å	35.9106(8)	30.4579(10)	19.7489(4)
α/°	90	90	104.8568(17)
β/°	91.6279(19)	97.629(3)	105.8861(17)
γ/°	90	90	105.3698(17)
Volume/Å^3	3629.97(13)	3341.12(17)	3490.89(13)
Z	8	4	2
ρ_{calc}g/cm^3	1.279	1.389	1.330
μ/mm^1	0.639	0.695	0.665
F(000)	1456.0	1456.0	1456.0
Crystal size/mm^3	0.27 × 0.03 × 0.02	0.47 × 0.03 × 0.03	0.35 × 0.22 × 0.05
Radiation	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)
2Θ range for data collection/°	6.718 to 153.178	5.362 to 153.366	4.976 to 153.572
Index ranges	$-28 \le h \le 33$, $-4 \le k \le 4$, $-44 \le l \le 45$	$-22 \le h \le 15$, $-7 \le k \le 7$, $-36 \le l \le 38$	$-14 \le h \le 14$, $-22 \le k \le 22$, $-23 \le l \le 24$
Reflections collected	13526	28071	58230
Independent reflections	3752 [R_{int} = 0.0199, R_{sigma} = 0.0183]	6938 [R_{int} = 0.0530, R_{sigma} = 0.0488]	14565 [R_{int} = 0.0281, R_{sigma} = 0.0249]
Data/restraints/parameters	3752/0/248	6938/0/488	14565/0/1054
Goodness-of-fit on F^2	1.032	1.049	1.016
Final R indexes [I>=2σ (I)]	R_1 = 0.0387, wR_2 = 0.1028	R_1 = 0.0517, wR_2 = 0.1270	R_1 = 0.0461, wR_2 = 0.1221
Final R indexes [all data]	R_1 = 0.0433, wR_2 = 0.1069	R_1 = 0.0702, wR_2 = 0.1408	R_1 = 0.0531, wR_2 = 0.1294
Largest diff. peak/hole / e Å^{-3}	0.33/-0.21	0.25/-0.23	0.69/-0.23

$R_1 = \Sigma \, ||Fo|-|Fc| \, / \, \Sigma \, |Fo|$; $wR_2 = [\Sigma \, (w(Fo^2 - Fc^2)^2 \, / \, \Sigma \, w(Fo^2)^2]^{1/2}$

Identification code	**2**	**2-a**
CCDC number	1572596	1572599
Empirical formula	$C_{47}H_{31.5}Ag_2B_2F_8N_{6.5}O_{2.5}$	$C_{50}H_{35}Ag_2F_6N_7O_9S_2$
Formula weight	1116.65	1271.71
Temperature/K	100.00(10)	100.01(10)
Crystal system	triclinic	monoclinic
Space group	P-1	$P2_1/c$
a/Å	13.5216(5)	12.72079(13)
b/Å	14.9223(6)	30.3305(3)
c/Å	21.6131(8)	13.47657(15)
α/°	87.526(3)	90
β/°	80.106(3)	112.9233(13)
γ/°	85.894(3)	90
Volume/Å^3	4283.0(3)	4789.01(10)
Z	4	4
ρ_{calc}/g/cm^3	1.732	1.764
μ/mm^1	8.088	8.168
F(000)	2220.0	2544.0
Crystal size/mm^3	0.15 × 0.07 × 0.06	0.43 × 0.20 × 0.12
Radiation	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)
2Θ range for data collection/°	5.94 to 153.36	5.828 to 152.83
Index ranges	-17 ≤ h ≤ 16, -18 ≤ k ≤ 18, -27 ≤ l ≤ 18	-15 ≤ h ≤ 13, -37 ≤ k ≤ 38, -15 ≤ l ≤ 16
Reflections collected	49184	40177
Independent reflections	17514 [R_{int} = 0.0348, R_{sigma} = 0.0385]	9982 [R_{int} = 0.0419, R_{sigma} = 0.0342]
Data/restraints/parameters	17514/6/1240	9982/0/689
Goodness-of-fit on F^2	1.039	1.055
Final R indexes [I>=2σ (I)]	R_1 = 0.0632, wR_2 = 0.1615	R_1 = 0.0305, wR_2 = 0.0794
Final R indexes [all data]	R_1 = 0.0827, wR_2 = 0.1768	R_1 = 0.0317, wR_2 = 0.0804
Largest diff. peak/hole / e Å^{-3}	3.25/-1.96	0.79/-1.00

$R_1 = \Sigma\ ||Fo|-|Fc|\ /\ \Sigma\ |Fo|$; $wR_2 = [\Sigma\ (w(Fo^2 - Fc^2)^2\ /\ \Sigma\ w(Fo^2)^2]^{1/2}$

Single crystals were mounted on a Mitegen loop using Paratone-N oil and were cooled under a stream of nitrogen. Figures and tables were generated using OLEX2.[1] Crystal data were collected on a Rigaku Oxford Diffraction SuperNova diffractometer using Cu Kα radiation; the structures were solved by direct methods using ShelXT[2] and refined by least squares using ShelXL.[3]

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. *42*, 339-341.

2. Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.

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