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Silver and gold luminescent metallomesogens based on pyrazole ligands

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SUPPLEMENTARY INFORMATION

Preparation of the complexes type I: $[Ag(Hpz^{2R(n)})_2][A]$ (R = $C_6H_4OC_nH_{2n+1}$, n = 12, 14, 16, 18; A = BF_4^- I_{BF4} (1-4), PF_6^- I_{PF6} (5-8), NO_3^- I_{NO3} (9-12).

To a solution of the corresponding 3,5-bis(4-alkyloxyphenyl)-1*H*-pyrazole ($Hpz^{2R(n)}$) in dry tetrahydrofurane was added AgA in a 2:1 molecular ratio under dinitrogen atmosphere. The mixture was stirred for 24 hours in absence of light, and then filtered through Celite. The clear filtrate was removed *in vacuo* and the residue was dissolved in dichloromethane. Addition of hexane gave rise to a colorless solid, which was filtered off, washed with hexane and dried *in vacuo*. Spectroscopic data are given for **1**, **5** and **9**. Data for the other homologues are essentially identical.

$[Ag(Hpz^{2R(12)})_2][BF_4]$ **(1)**. ν_{max}/cm^{-1} 3223m (NH), 1615m (C=N) + (C=C), 1026s (BF). δ_H (300 MHz; $CDCl_3$; Me_4Si) 0.88 (12 H, t, $^3J_{H,H}$ 6.5, CH_3), 1.27 (72 H, m, CH_2), 1.80 (8 H, m, CH_2), 3.96 (8 H, t, $^3J_{H,H}$ 6.3, OCH_2), 6.67 (2 H, s, C(4)H), 6.88 (8 H, d, $^3J_{H,H}$ 8.5, H_m), 7.60 (8 H, d, $^3J_{H,H}$ 8.5, H_o).

$[Ag(Hpz^{2R(12)})_2][PF_6]$ **(5)**. ν_{max}/cm^{-1} 3395m (NH), 1615m (C=N) + (C=C), 838vs (PF). δ_H (300 MHz; $CDCl_3$; Me_4Si) 0.88 (12 H, t, $^3J_{H,H}$ 6.6, CH_3), 1.25 (72 H, m, CH_2), 1.80 (8 H, m, $^3J_{H,H}$ 6.8, CH_2), 3.96 (8 H, t, $^3J_{H,H}$ 6.3, OCH_2), 6.68 (2 H, s, C(4)H), 6.87 (8 H, d, $^3J_{H,H}$ 8.5, H_m), 7.60 (8 H, d, $^3J_{H,H}$ 8.5, H_o).

$[Ag(Hpz^{2R(12)})_2][NO_3]$ **(9)**. ν_{max}/cm^{-1} 3223m (NH), 1615m (C=N) + (C=C), 1388m (NO). δ_H (300 MHz; $CDCl_3$; Me_4Si) 0.88 (12 H, t, $^3J_{H,H}$ 6.8, CH_3), 1.27 (72 H, m, CH_2), 1.81 (8 H, m, $^3J_{H,H}$ 7.0, CH_2), 3.99 (8 H, t, $^3J_{H,H}$ 6.6, OCH_2), 6.70 (2 H, s, C(4)H), 6.92 (8 H, d, $^3J_{H,H}$ 8.6, H_m), 7.69 (8 H, d, $^3J_{H,H}$ 8.6, H_o).

Preparation of the complexes type II: $[Au(Hpz^{2R(n)})_2][A]$ (R = $C_6H_4OC_nH_{2n+1}$, n = 12, 14; A = BF_4^- II_{BF4} (13, 14), PF_6^- II_{PF6} (15, 16), NO_3^- II_{NO3} (17, 18).

To a mixture of AgA and [AuCl(tht)] in dry tetrahydrofurane was added a solution of the corresponding 3,5-bis(4-alkyloxyphenyl)-1*H*-pyrazole ($Hpz^{2R(n)}$) in a 1:1:2 molecular ratio under dinitrogen atmosphere. The mixture was stirred for 24 hours in absence of light, and then filtered through Celite. The clear filtrate was removed *in vacuo* and the residue was dissolved in dichloromethane. Addition of hexane gave rise to a colorless solid, which was filtered off, washed with hexane and dried *in vacuo*. Spectroscopic data are given for **13**, **15** and **17**. Data for the other homologues are essentially identical.

$[Au(Hpz^{2R(12)})_2][BF_4]$ **(13)**. ν_{max}/cm^{-1} 3246m (NH), 1580m (C═N) + (C═C), 1041s (BF). δ_H (300 MHz; $CDCl_3$; Me_4Si) 0.88 (12 H, t, $^3J_{H,H}$ 6.2, CH_3), 1.28 (72 H, m, CH_2), 1.82 (8 H, m, $^3J_{H,H}$ 6.2, CH_2), 3.96 (4 H, t, $^3J_{H,H}$ 6.2, OCH_2), 4.00 (4 H, t, $^3J_{H,H}$ 6.7, OCH_2), 6.74 (2 H, s, C(4)H), 6.79 (4 H, d, $^3J_{H,H}$ 8.8, H_m), 7.01 (4 H, d, $^3J_{H,H}$ 8.4, H_m), 7.69 (4 H, d, $^3J_{H,H}$ 8.8, H_o), 7.71 (4 H, d, $^3J_{H,H}$ 8.4, H_o), 12.49 (2 H, s, NH).

$[Au(Hpz^{2R(12)})_2][PF_6]$ **(15)**. ν_{max}/cm^{-1} 3390m (NH), 1626m (C═N) + (C═C), 836vs (PF). δ_H (300 MHz; $CDCl_3$; Me_4Si) 0.88 (12 H, t, $^3J_{H,H}$ 7.0, CH_3), 1.28 (72 H, m, CH_2), 1.81 (8 H, m, CH_2), 3.93 (8 H, t, $^3J_{H,H}$ 6.4, OCH_2), 6.70 (2 H, s, C(4)H), 6.75 (4 H, d, $^3J_{H,H}$ 8.8, H_m), 7.0 (4 H, d, $^3J_{H,H}$ 8.8, H_m), 7.75 (4 H, d, $^3J_{H,H}$ 8.8, H_o), 7.79 (4 H, d, $^3J_{H,H}$ 8.8, H_o), 13.85 (2 H, s, NH).

$[Au(Hpz^{2R(12)})_2][NO_3]$ **(17)**. ν_{max}/cm^{-1} 3230m (NH), 1615m (C═N) + (C═C), 1385m (NO). δ_H (300 MHz; $CDCl_3$; Me_4Si) 0.88 (12 H, t, $^3J_{H,H}$ 6.8, CH_3), 1.27 (72 H, m, CH_2), 1.81 (8 H, m, CH_2), 3.97 (4 H, t, $^3J_{H,H}$ 6.2, OCH_2), 4.00 (4 H, t, $^3J_{H,H}$ 6.1, OCH_2), 6.74 (2 H, s, C(4)H), 6.81 (4 H, d, $^3J_{H,H}$ 8.7, H_m), 7.01 (4 H, d, $^3J_{H,H}$ 8.1, H_m), 7.75 (4 H, d, $^3J_{H,H}$ 8.7, H_o), 7.79 (4 H, d, $^3J_{H,H}$ 8.1, H_o), 13.85 (2 H, s, NH).

Preparation of the complexes type III: $[Ag(Hpz^{R(n)})_2][A]$ (R = $C_6H_4OC_nH_{2n+1}$, n = 4, 12, 14, 16, 18; A = BF_4^- III_{BF4} (19-22), PF_6^- III_{PF6} (23-27), NO_3^- III_{NO3} (28-31).

To a solution of the corresponding 3-(4-alkyloxyphenyl)-1*H*-pyrazole ($Hpz^{R(n)}$) in dry tetrahydrofurane was added AgA in a 2:1 molecular ratio under dinitrogen atmosphere. The mixture was stirred for 24 hours in absence of light, and then filtered through Celite. The clear filtrate was removed *in vacuo* and the residue was dissolved in dichloromethane. Addition of hexane gave rise to a colorless solid, which was filtered off, washed with hexane and dried *in vacuo*. Spectroscopic data are given for **19**, **23, 24** and **28**. Data for the other homologues are essentially identical.

$[Ag(Hpz^{R(12)})_2][BF_4]$ **(19)**. ν_{max}/cm^{-1} 3231m (NH), 1618m (C=N) + (C=C), 1032s (BF). δ_H(300 MHz; $CDCl_3$; Me_4Si) 0.87 (6 H, t, $^3J_{H,H}$ 6.8, CH_3), 1.25 (36 H, m, CH_2), 1.80 (4 H, m, $^3J_{H,H}$ 6.8, CH_2), 3.99 (4 H, t, $^3J_{H,H}$ 6.6, OCH_2), 6.57 (2 H, d, $^3J_{H,H}$ 2.2, C(4)H), 6.94 (4 H, d, $^3J_{H,H}$ 8.8, H_m), 7.64 (2 H, br, C(5)H), 7.66 (4 H, d, $^3J_{H,H}$ 8.8, H_o).

$[Ag(Hpz^{R(4)})_2][PF_6]$ **(23).** ν_{max}/cm^{-1} 3370m (NH), 1617m (C=N) + (C=C), 831vs (PF). δ_H(300 MHz; $CDCl_3$; Me_4Si) 0.99 (6 H, t, $^3J_{H,H}$ 7.2, CH_3), 1.48 (4 H, m, $^3J_{H,H}$ 6.9, CH_2), 1.79 (4 H, m, $^3J_{H,H}$ 6.9, CH_2), 3.98 (4 H, t, $^3J_{H,H}$ 6.4, OCH_2), 6.55 (2 H, d, $^3J_{H,H}$ 2.3, C(4)H), 6.94 (4 H, d, $^3J_{H,H}$ 8.3, H_m), 7.61 (2 H, br, C(5)H), 7.62 (4 H, d, $^3J_{H,H}$ 8.3, H_o).

$[Ag(Hpz^{R(12)})_2][PF_6]$ **(24)**. ν_{max}/cm^{-1} 3377m (NH), 1616m (C=N) + (C=C), 852vs (PF). δ_H(300 MHz; $CDCl_3$; Me_4Si) 0.88 (6 H, t, $^3J_{H,H}$ 6.6, CH_3), 1.27 (36 H, m, CH_2), 1.81 (4 H, m, $^3J_{H,H}$ 6.3, CH_2), 3.98 (4 H, t, $^3J_{H,H}$ 6.1, OCH_2), 6.56 (2 H, br, C(4)H), 6.94 (4 H, d, $^3J_{H,H}$ 8.3, H_m), 7.57 (4 H, d, $^3J_{H,H}$ 8.3, H_o), 7.65 (2 H, br, C(5)H).

$[Ag(Hpz^{R(12)})_2][NO_3]$ **(28)**. ν_{max}/cm^{-1} 3246m (NH), 1614m (C=N) + (C=C), 1380m (NO). δ_H(300 MHz; $CDCl_3$; Me_4Si) 0.89 (6 H, t, $^3J_{H,H}$ 6.6, CH_3), 1.28 (36 H, m, CH_2),

1.81 (4 H, m, $^3J_{H,H}$ 6.6, CH_2), 3.99 (4 H, t, $^3J_{H,H}$ 6.6, OCH_2), 6.55 (2 H, d, $^3J_{H,H}$ 1.9, C(4)H), 6.94 (4 H, d, $^3J_{H,H}$ 8.8, H_m), 7.64 (2 H, br, C(5)H), 7.66 (4 H, d, $^3J_{H,H}$ 8.8, H_o).

Preparation of the complexes type IV: $[Au(Hpz^{R(n)})_2][A]$ (R = $C_6H_4OC_nH_{2n+1}$, n = 12, 14; A = BF_4^- IV_{BF4} (33, 34), PF_6^- IV_{PF6} (35, 36), NO_3^- IV_{NO3} (37, 38).

To a mixture of AgA and [AuCl(tht)] in dry tetrahydrofurane was added a solution of the corresponding 3-(4-alkyloxyphenyl)-1*H*-pyrazole ($Hpz^{R(n)}$) in a 1:1:2 molecular ratio under dinitrogen atmosphere. The mixture was stirred for 24 hours in absence of light, and then filtered through Celite. The clear filtrate was removed *in vacuo* and the residue was dissolved in dichloromethane. Addition of hexane gave rise to a colorless solid, which was filtered off, washed with hexane and dried *in vacuo*. Spectroscopic data are given for **33**, **35** and **37**. Data for the other homologues are essentially identical.

$[Au(Hpz^{R(12)})_2][BF_4]$ **(33)**. ν_{max}/cm^{-1} 3247m (NH), 1581m (C═N) + (C═C), 1030s (BF). δ_H (300 MHz; $CDCl_3$; Me_4Si) 0.88 (6 H, t, $^3J_{H,H}$ 7.3, CH_3), 1.27 (36 H, m, CH_2), 1.80 (4 H, m, $^3J_{H,H}$ 7.3, CH_2), 3.99 (4 H, t, $^3J_{H,H}$ 6.4, OCH_2), 6.70 (2 H, br, C(4)H), 6.99 (4 H, d, $^3J_{H,H}$ 8.1, H_m), 7.72 (4 H, d, $^3J_{H,H}$ 8.1, H_o), 7.89 (2 H, br, C(5)H).

$[Au(Hpz^{R(12)})_2][PF_6]$ **(35)**. ν_{max}/cm^{-1} 3354m (NH), 1617m (C═N) + (C═C), 836vs (PF). δ_H (300 MHz; $CDCl_3$; Me_4Si) 0.88 (6 H, t, $^3J_{H,H}$ 6.7, CH_3), 1.26 (36 H, m, CH_2), 1.80 (4 H, m, $^3J_{H,H}$ 7.8, CH_2), 3.97 (4 H, t, $^3J_{H,H}$ 6.6, OCH_2), 6.64 (2 H, br, C(4)H), 6.99 (4 H, d, $^3J_{H,H}$ 8.7, H_m), 7.62 (4 H, d, $^3J_{H,H}$ 8.7,H_o), 7.84 (2 H, br, C(5)H).

$[Au(Hpz^{R(12)})_2][NO_3]$ **(37)**. ν_{max}/cm^{-1} 3230m (NH), 1579m (C═N) + (C═C), 1380m (NO). δ_H (300 MHz; $CDCl_3$; Me_4Si) 0.88 (6 H, t, $^3J_{H,H}$ 7.1, CH_3), 1.27 (36, m, CH_2), 1.80 (4 H, m, $^3J_{H,H}$ 7.7, CH_2), 3.99 (4 H, t, $^3J_{H,H}$ 6.4, OCH_2), 6.74 (2 H, br, C(4)H), 6.96 (4 H, d, $^3J_{H,H}$ 7.7, H_m), 7.65 (4 H, d, $^3J_{H,H}$ 7.6, H_o), 7.81 (2 H, br, C(5)H).

Table S1. Yields and analytical data of the compounds

COMPLEX		MOLECULAR FORMULA	Yield(%)	molecular weight ($gmol^{-1}$)	Elemental analysis calculated (%)			Elemental analysis experimental (%)		
					C	H	N	C	H	N
I_{BF4}	**1**	$C_{78}H_{120}N_4O_4AgBF_4$	55	1372.5	68.3	8.8	4.1	68.3	8.6	4.1
	2	$C_{86}H_{136}N_4O_4AgBF_4$	56	1484.7	69.6	9.2	3.8	69.9	9.3	3.5
	3	$C_{94}H_{152}N_4O_4AgBF_4$	65	1596.0	70.7	9.6	3.5	70.4	9.4	3.4
	4	$C_{102}H_{168}N_4O_4AgBF_4$	68	1709.0	71.7	9.9	3.3	71.5	9.6	3.2
I_{PF6}	**5**	$C_{78}H_{120}N_4O_4AgPF_6$	53	1430.7	65.5	8.4	3.9	65.6	8.1	3.9
	6	$C_{86}H_{136}N_4O_4AgPF_6$	56	1542.9	66.9	8.9	3.6	66.8	8.6	3.6
	7	$C_{94}H_{152}N_4O_4AgPF_6$	50	1655.1	68.2	9.3	3.4	68.0	9.3	3.3
	8	$C_{102}H_{168}N_4O_4AgPF_6$	54	1767.3	69.3	9.6	3.2	69.5	9.3	3.2
I_{NO3}	**9**	$C_{78}H_{120}N_4O_4AgNO_3$	53	1347.7	69.5	9.0	5.2	69.4	8.8	5.0
	10	$C_{86}H_{136}N_4O_4AgNO_3$	56	1459.9	70.7	9.4	4.8	70.5	9.2	4.8
	11	$C_{94}H_{152}N_4O_4AgNO_3$	51	1572.2	71.8	9.8	4.4	72.0	9.6	4.2
	12	$C_{102}H_{168}N_4O_4AgNO_3$	55	1684.4	72.7	10.0	4.2	72.4	9.6	4.2
II_{BF4}	**13**	$C_{78}H_{120}N_4O_4AuBF_4$	48	1461.6	64.1	8.3	3.8	64.5	8.4	3.6
	14	$C_{86}H_{136}N_4O_4AuBF_4$	50	1573.8	65.6	8.7	3.6	65.8	8.6	3.3
II_{PF6}	**15**	$C_{78}H_{120}N_4O_4AuPF_6$	56	1519.8	61.6	8.0	3.7	61.3	7.7	3.4
	16	$C_{86}H_{136}N_4O_4AuPF_6$	54	1632.0	63.3	8.4	3.4	63.6	8.7	3.3
II_{NO3}	**17**	$C_{78}H_{120}N_4O_4AuNO_3$	60	1436.8	65.2	8.4	4.9	65.1	8.2	4.7
	18	$C_{86}H_{136}N_4O_4AuNO_3$	61	1549.0	66.7	8.8	4.5	66.3	8.7	4.8
III_{BF4}	**19**	$C_{42}H_{64}N_4O_2AgBF_4$	51	851.7	59.2	7.6	6.6	59.4	7.4	6.5
	20	$C_{46}H_{72}N_4O_2AgBF_4$	56	907.8	60.9	8.0	6.2	60.9	8.1	6.1
	21	$C_{50}H_{80}N_4O_2AgBF_4$	60	963.9	62.3	8.4	5.8	62.0	8.3	5.6
	22	$C_{54}H_{88}N_4O_2AgBF_4$	62	1020.0	63.6	8.7	5.5	63.6	8.4	5.3
III_{PF6}	**23**	$C_{26}H_{32}N_4O_2AgPF_6$	68	685.4	45.6	4.7	8.2	45.6	4.6	8.2
	24	$C_{42}H_{64}N_4O_2AgPF_6$	57	909.8	55.4	7.1	6.2	55.0	7.1	6.5
	25	$C_{46}H_{72}N_4O_2AgPF_6$	55	965.9	57.2	7.5	5.8	57.5	7.3	5.8
	26	$C_{50}H_{80}N_4O_2AgPF_6$	55	1022.0	58.8	7.9	5.5	58.7	7.9	5.4
	27	$C_{54}H_{88}N_4O_2AgPF_6$	60	1078.2	60.2	8.2	5.2	60.0	8.2	4.8
III_{NO3}	**28**	$C_{42}H_{64}N_4O_2AgNO_3$	51	826.9	61.0	7.8	8.5	61.0	7.5	8.4
	29	$C_{46}H_{72}N_4O_2AgNO_3$	53	883.0	62.6	8.2	7.9	62.5	8.1	8.0
	30	$C_{50}H_{80}N_4O_2AgNO_3$	50	939.1	63.9	8.6	7.5	63.7	8.6	7.5
	31	$C_{54}H_{88}N_4O_2AgNO_3$	50	995.2	65.2	8.9	7.0	65.0	8.8	7.0
	32	$C_{26}H_{32}N_4O_2AgPO_2F_2$	-	641.4	48.7	5.0	8.7	48.8	5.0	8.8
IV_{BF4}	**33**	$C_{42}H_{64}N_4O_2AuBF_4$	66	940.8	53.6	6.9	6.0	53.2	7.0	6.2
	34	$C_{46}H_{72}N_4O_2AuBF_4$	67	996.9	55.4	7.3	5.6	55.3	7.1	5.7
IV_{PF6}	**35**	$C_{42}H_{64}N_4O_2AuPF_6$	65	998.9	50.5	6.5	5.6	50.1	6.3	5.3
	36	$C_{46}H_{72}N_4O_2AuPF_6$	68	1055.0	52.4	6.9	5.3	52.2	6.3	5.2
IV_{NO3}	**37**	$C_{42}H_{64}N_4O_2AuNO_3$	68	916.0	55.1	7.0	7.6	54.9	6.9	7.4
	38	$C_{46}H_{72}N_4O_2AuNO_3$	66	972.1	56.8	7.5	7.2	56.7	7.5	7.0
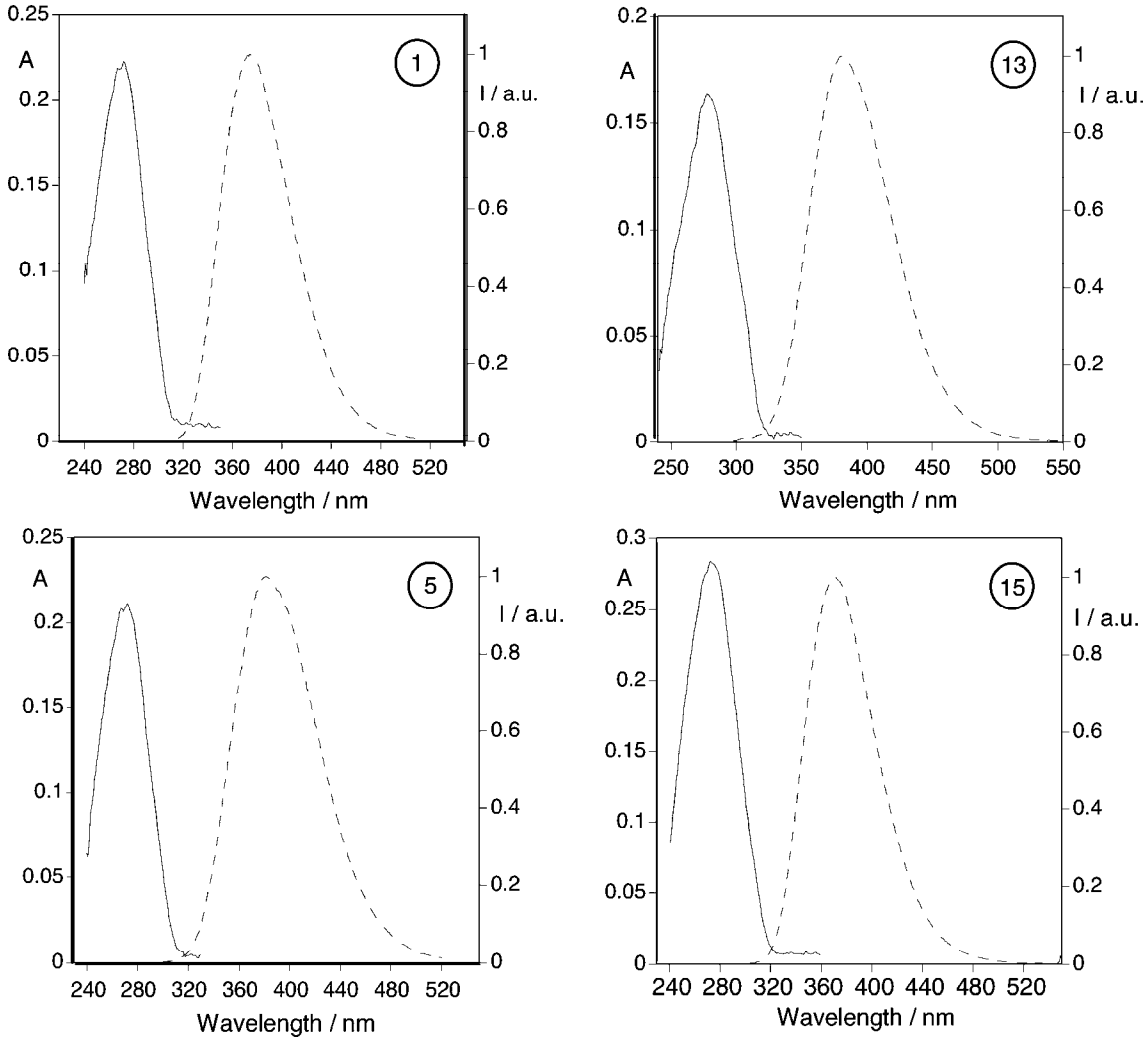
Figure S1: Absorption and normalized fluorescence emission spectra of compounds **1**, **5**, **13** and **15** in freshly chloroform solution at concentrations 2.84E^{-6} M (**1**), 2.51E^{-6} M (**5**), 2.08E^{-6} M (**13**) and 3.30E^{-6} M (**15**) (λ_{exc} = 274 nm; Room Temperature)