Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Novel fluorescent anthracene-bodipy dyads displaying sensitivity to pH and turn-on behaviour towards Cu (II) ions

A. Vanessa Saura,[1] M. Isabel Burguete,[1] Francisco Galindo,*[,1] Santiago V. Luis*[,1]

E-mail: francisco.galindo@uji.es, luiss@uji.es

[1] Departamento de Química Inorgánica y Orgánica, Universitat Jaume I, Av. Sos Baynat s/n, E-12071 Castellón (Spain)

Supporting Information

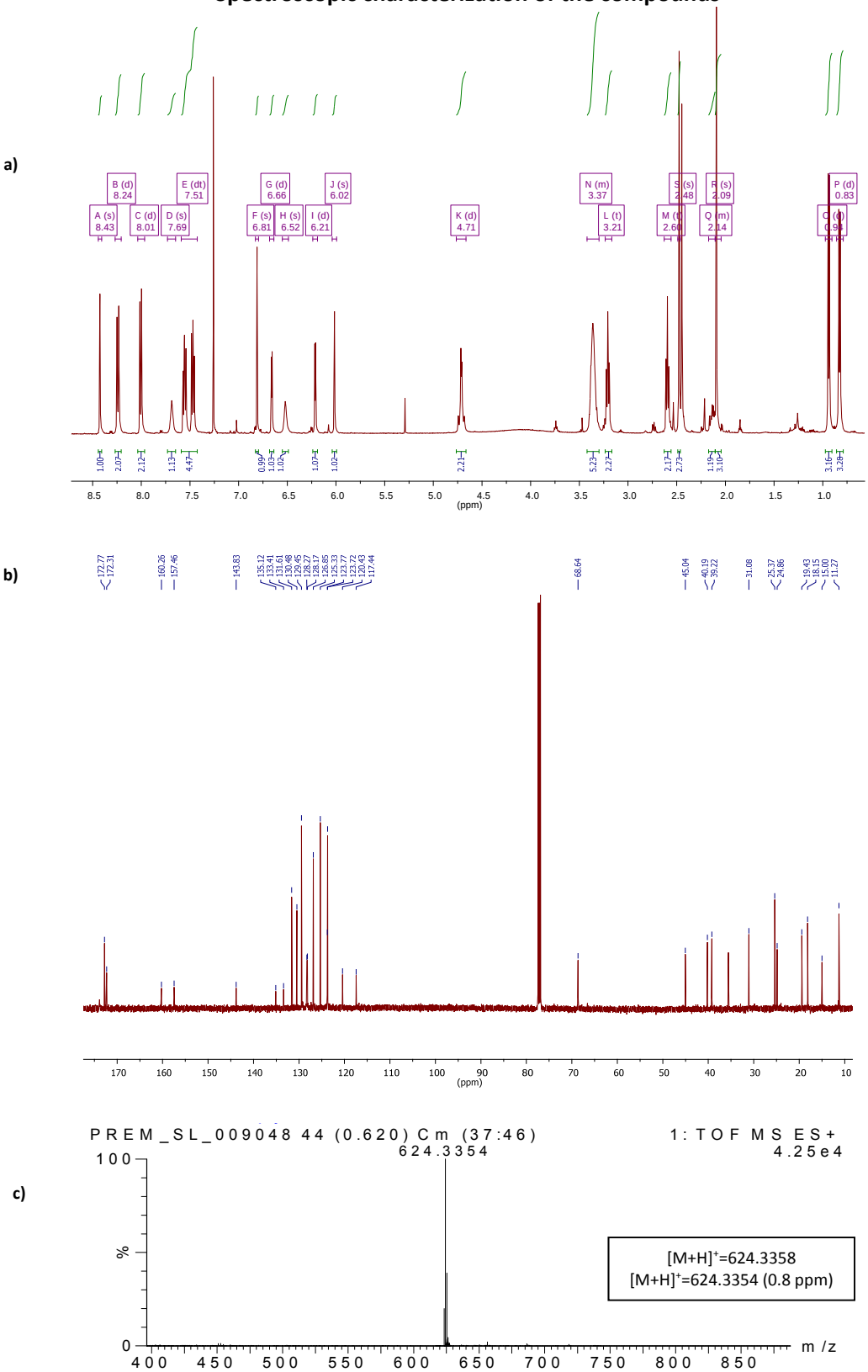

Figure S1. a) ^{1}H-NMR spectrum in $CHCl_3$-*d*, **b)** ^{13}C-NMR spectrum in $CHCl_3$-*d* and **c)** ESI-TOF spectrum of compound **1a**.

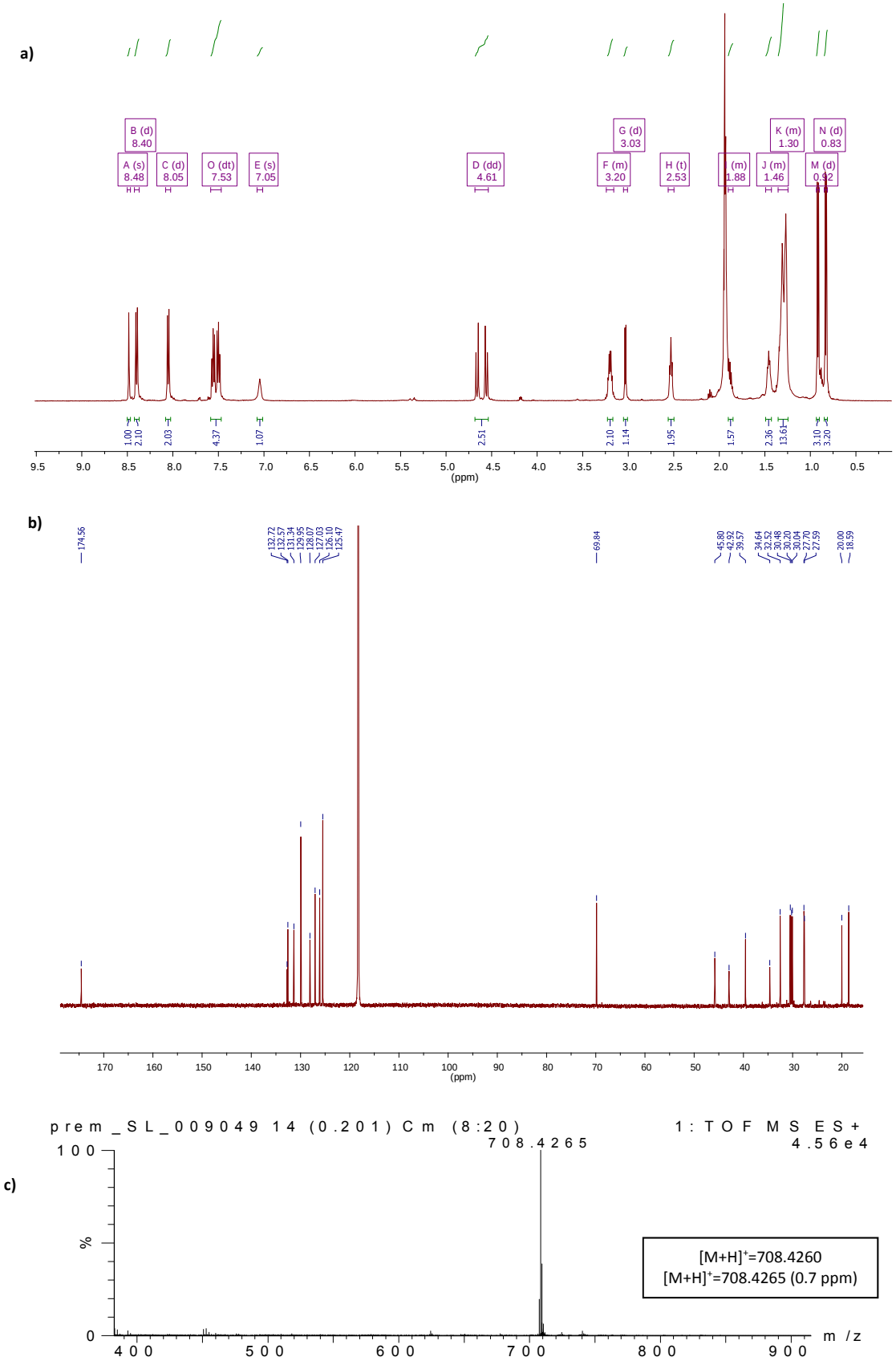

Figure S2. a) ^{1}H-NMR spectrum in CH_3CN-d_3, **b)** ^{13}C-NMR spectrum in CH_3CN-d_3 and **c)** ESI-TOF spectrum of compound **1b**.

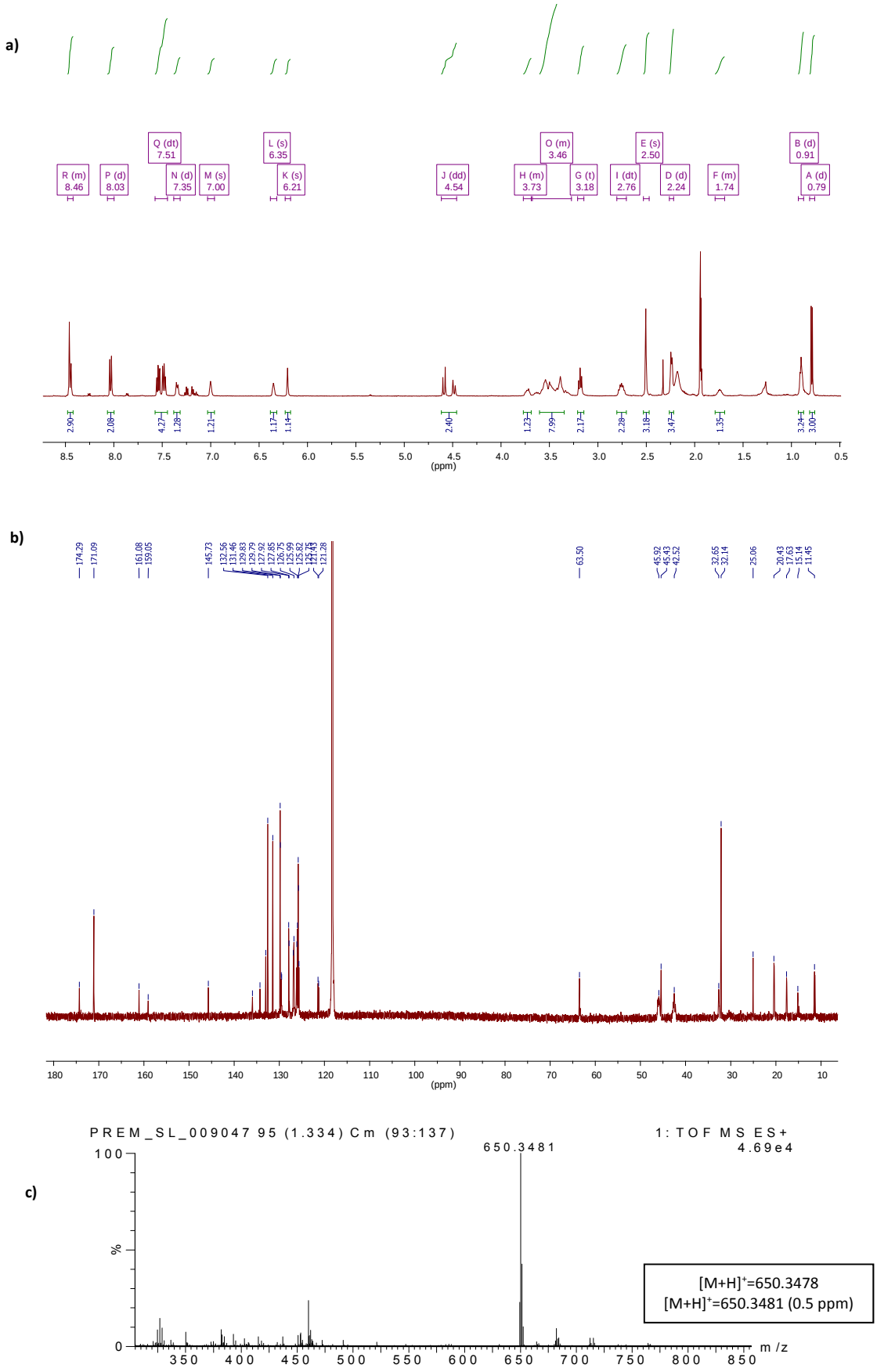

Figure S3. a) ^{1}H-NMR spectrum in CH_3CN-d_3, **b)** ^{13}C-NMR spectrum in CH_3CN-d_3 and **c)** ESI-TOF spectrum of compound **1c**.

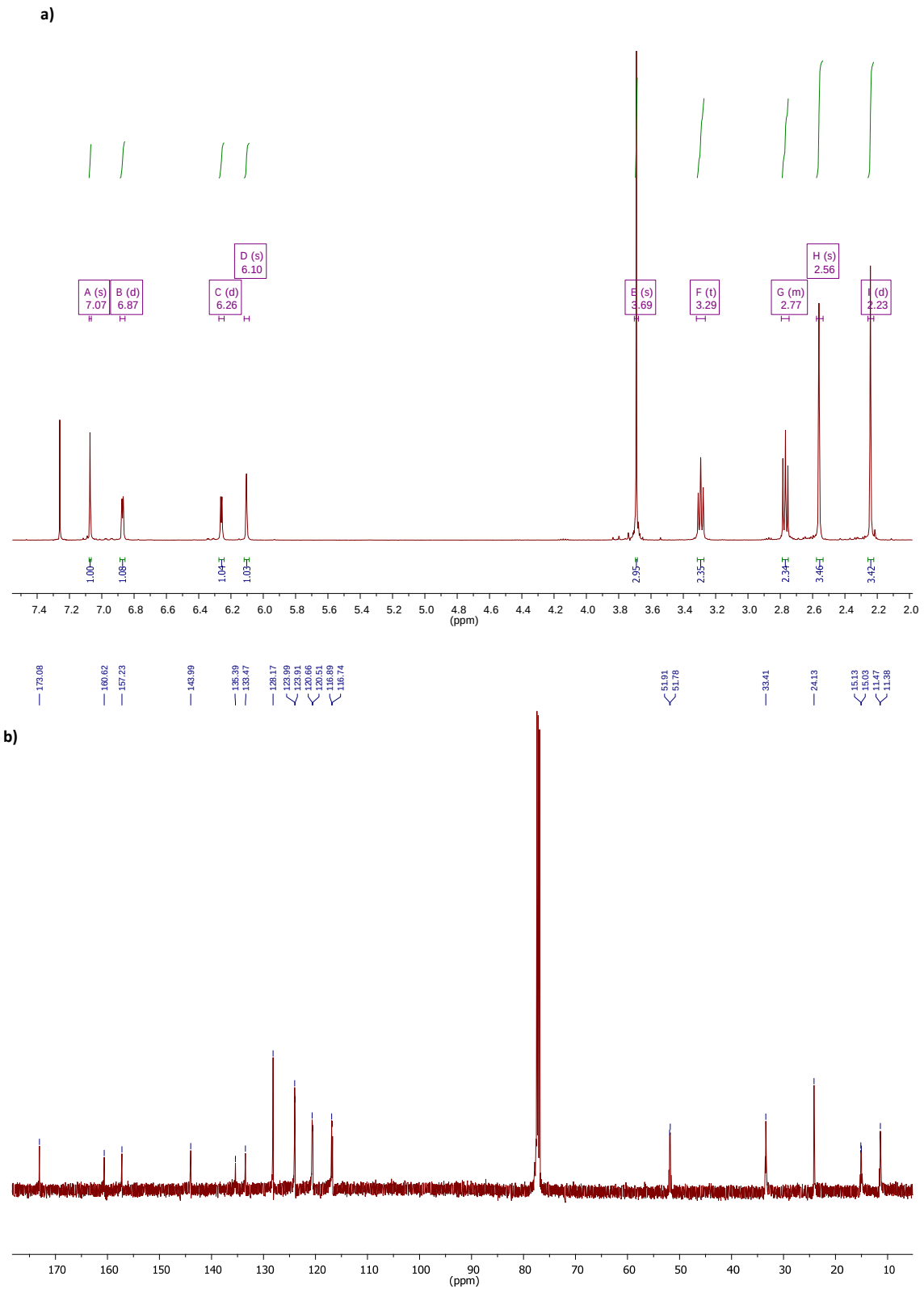

Figure S4. a) ^{1}H-NMR spectrum in $CHCl_3$-*d* and **b)** ^{13}C-NMR spectrum and in $CHCl_3$-*d* of model compound **3**.

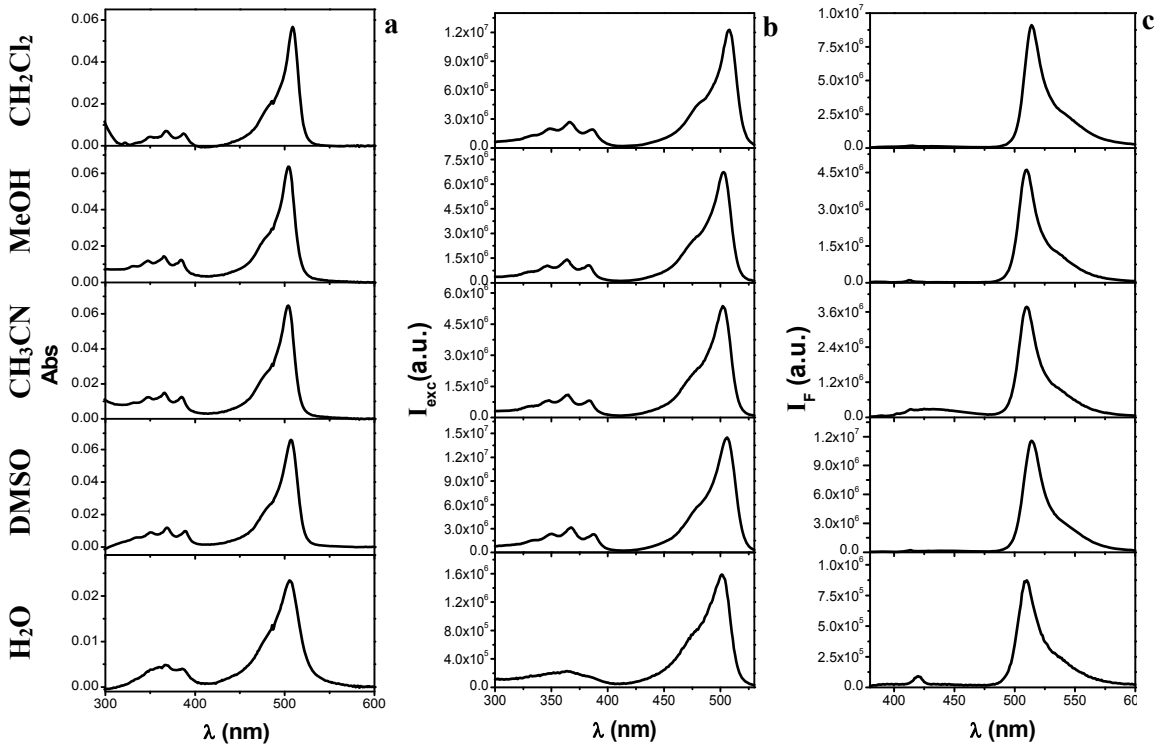

Figure S5. Photophysical characterization of compound **1a** ($1 \cdot 10^{-6}$M) in different media, from top to bottom: CH_2Cl_2, MeOH, CH_3CN, DMSO, H_2O. **a)** Absorption spectra; **b)** excitation spectra (λ_{exc}=540nm); **c)** emission spectra (λ_{exc}=368nm). Measurement solutions prepared from concentrated stock ($1 \cdot 10^{-3}$M) of **1a** in DMSO.

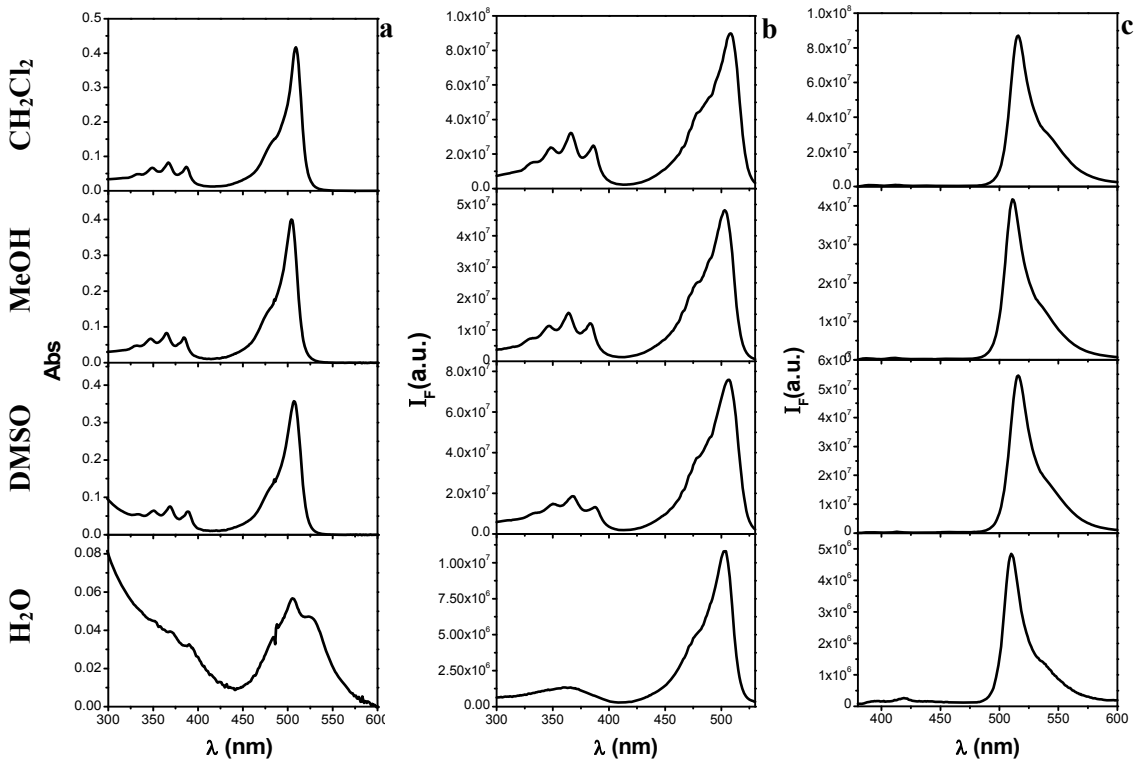

Figure S6. Photophysical characterization of compound **1b** ($5 \cdot 10^{-6}$M) in different media, from top to bottom: CH_2Cl_2, MeOH, DMSO, H_2O.* **a)** Absorption spectra; **b)** excitation spectra (λ_{exc}=540nm); **c)** emission spectra (λ_{exc}=368nm). Measurement solutions prepared from concentrated stock ($1 \cdot 10^{-3}$M) of **1b** in DMSO.

* In that case it was not possible to perform measurements in water due to compound low solubility in that media. Addition of MeOH (10%) to the media facilitated compound dissolution.

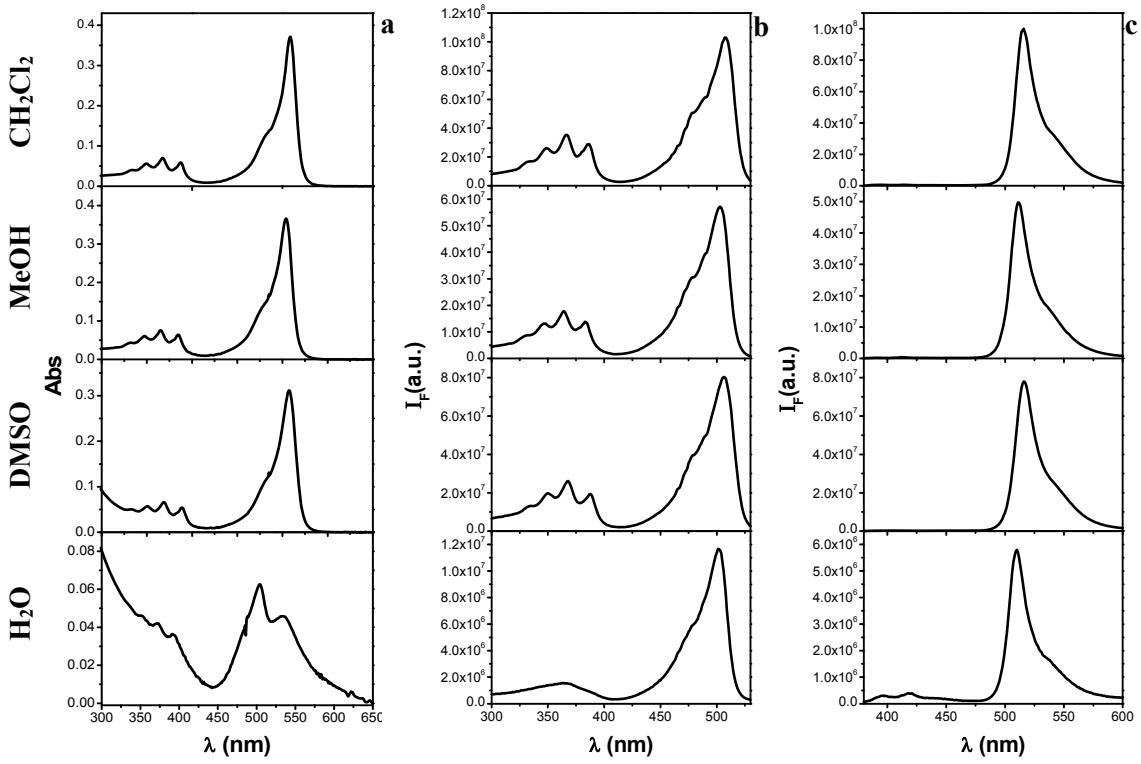

Figure S7. Photophysical characterization of compound **1c** ($5 \cdot 10^{-6}$M) in different media, from top to bottom: CH_2Cl_2, MeOH, DMSO, H_2O.* **a)** absorption spectra; **b)** excitation spectra (λ_{exc}=540nm); **c)** emission spectra (λ_{exc}=368nm). Measurement solutions prepared from concentrated stock ($1 \cdot 10^{-3}$M) of **1c** in DMSO.

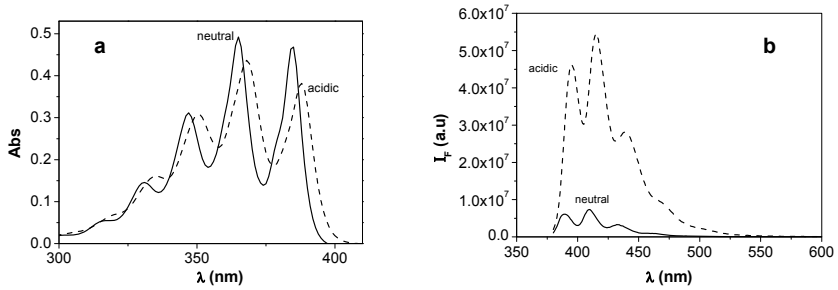

Figure S8. Photophysical characterization of compound **2** ($5.6 \cdot 10^{-5}$ M) in MeOH (**–**) and MeOH with an excess of TFA (---). **a)** Absorption spectra and **b)** emission spectra (λ_{exc}=375nm). Measurement solution prepared from concentrated stock ($1 \cdot 10^{-3}$ M) of **2** in MeOH.

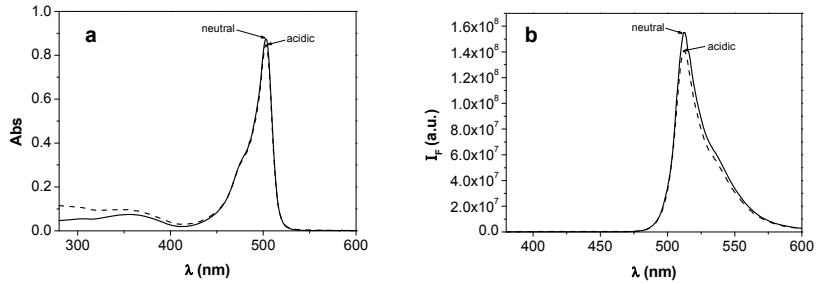

Figure S9. Photophysical characterization of compound **3** ($1 \cdot 10^{-5}$M) in MeOH (**–**) and MeOH with an excess of TFA (---). **a)** Absorption spectra and **b)** emission spectra (λ_{exc}=375nm). Measurement solution prepared from concentrated stock ($1 \cdot 10^{-3}$M) of **3** in MeOH.

Table S1. Photophysical characterization of compounds **1a**-**1c** and its corresponding model compounds **2** and **3** in different media.

	Solv.	Abs λ(nm)	Exc λ(nm)	Emis λ(nm)	ϕ_F[a]	τ (ns)[b]	SS (nm)
1a	CH_2Cl_2	349, 368, 387, 509	348, 366, 386, 508	514			146
	MeOH	347, 365, 385, 504	346, 364, 384, 503	510	0.06	0.8 (53 %), 5.6 (47 %)[c] 1.7 (56 %), 5.0(44 %)[d]	142
	CH_3CN	347, 366, 385, 504	346, 364, 384, 502	510			142
	DMSO	350, 369, 389, 507	350, 368, 388, 506	514			146
	H_2O	359, 368, 386, 506	365, 501	420, 510			142
1b	CH_2Cl_2	349, 367, 387, 509	348, 366, 386, 508	516			148
	MeOH	347, 365, 385, 504	347, 364, 384, 503	512	0.21	0.5 (76 %), 2.2 (24 %)[c] 2.0(80 %), 4.3 (20 %)[d]	144
	DMSO	350, 369, 389, 507	350, 368, 388, 506	516			148
	H_2O	351, 370, 390, 506, 527	365, 503	419, 510			142
1c	CH_2Cl_2	349, 367, 387, 509	349, 366, 386, 508	516			148
	MeOH	347, 365, 385, 504	346, 364, 384, 503	512	0.23	0.7 (81 %), 3.9 (19 %)[c] 5.8[d]	144
	DMSO	350, 369, 389, 507	350, 368, 388, 506	516			148
	H_2O	353, 371, 392, 506, 528	365, 502	419, 510			142
2	MeOH	347, 365, 385	--	389, 410, 435	0.06	7.3[c]	35
3	MeOH	355, 503	--	512	0.75	6.4[d]	9

[a] Fluorescence quantum yield. [b] fluorescence lifetime. [c] Lifetime recorded at 420 nm, corresponding to anthracene unit. [d] Lifetime recorded at 510 nm, corresponding to bodipy unit. Excitación spectra (λ_{emis}=540 nm). Emisión spectra (λ_{exc}=368 nm). Lifetime (λ_{exc}=372 nm).

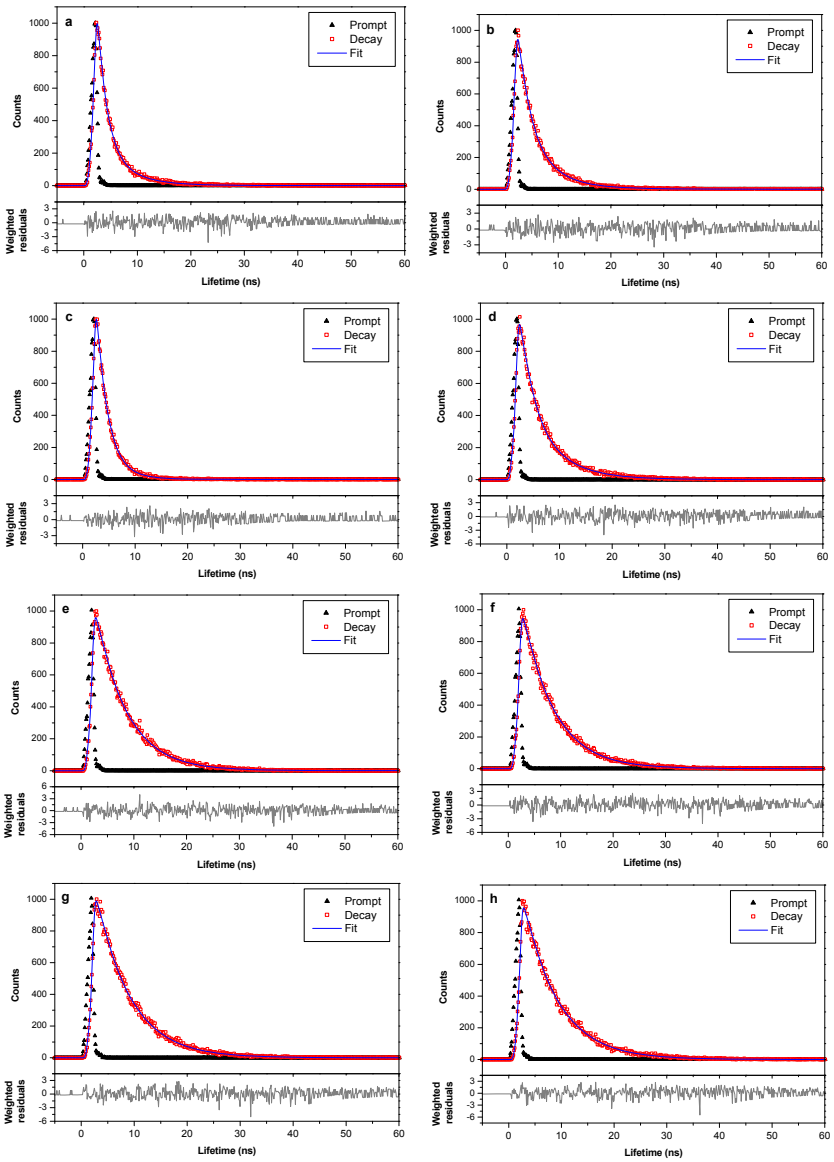

Figure S10. Fluorescence decay curves of **1a-c** and **3** ($1 \cdot 10^{-5}$ M). **a, c, e** and **g)** in MeOH; **b, d, f** and **h)** in MeOH with addition of an excess of trifluoroacetic acid. Only the emission from the bodipy unit is presented, emission from anthracene moiety was very weak in all cases due to EET. λ_{exc}=372 nm. Bodipy moiety life time emission was recorded at 510 nm.

Fluorescent pH titrations of 1a and 1b

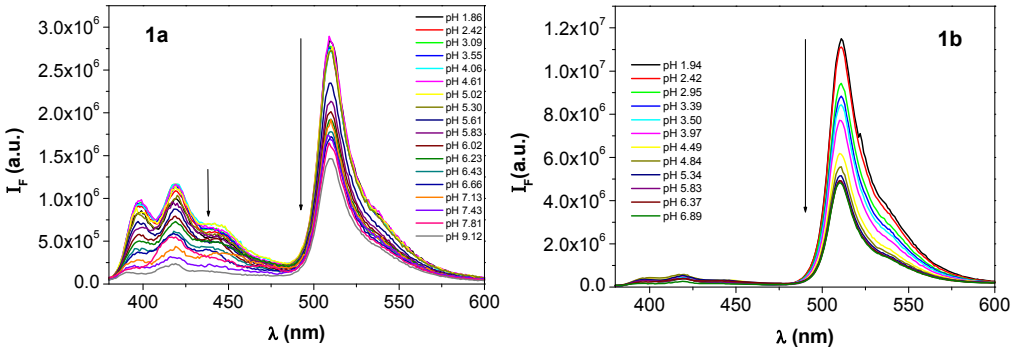

Figure S11. Fluorescence pH titration of compounds **1a** and **1b** ($5 \cdot 10^{-6}$ M) in aqueous medium: 0.1 M PBS buffered solution containing 1.25% DMSO (from concentrated stock solution). λ_{exc}=368 nm.

Influence of metallic cations on the fluorescent acid-base behavior of 1a-1c

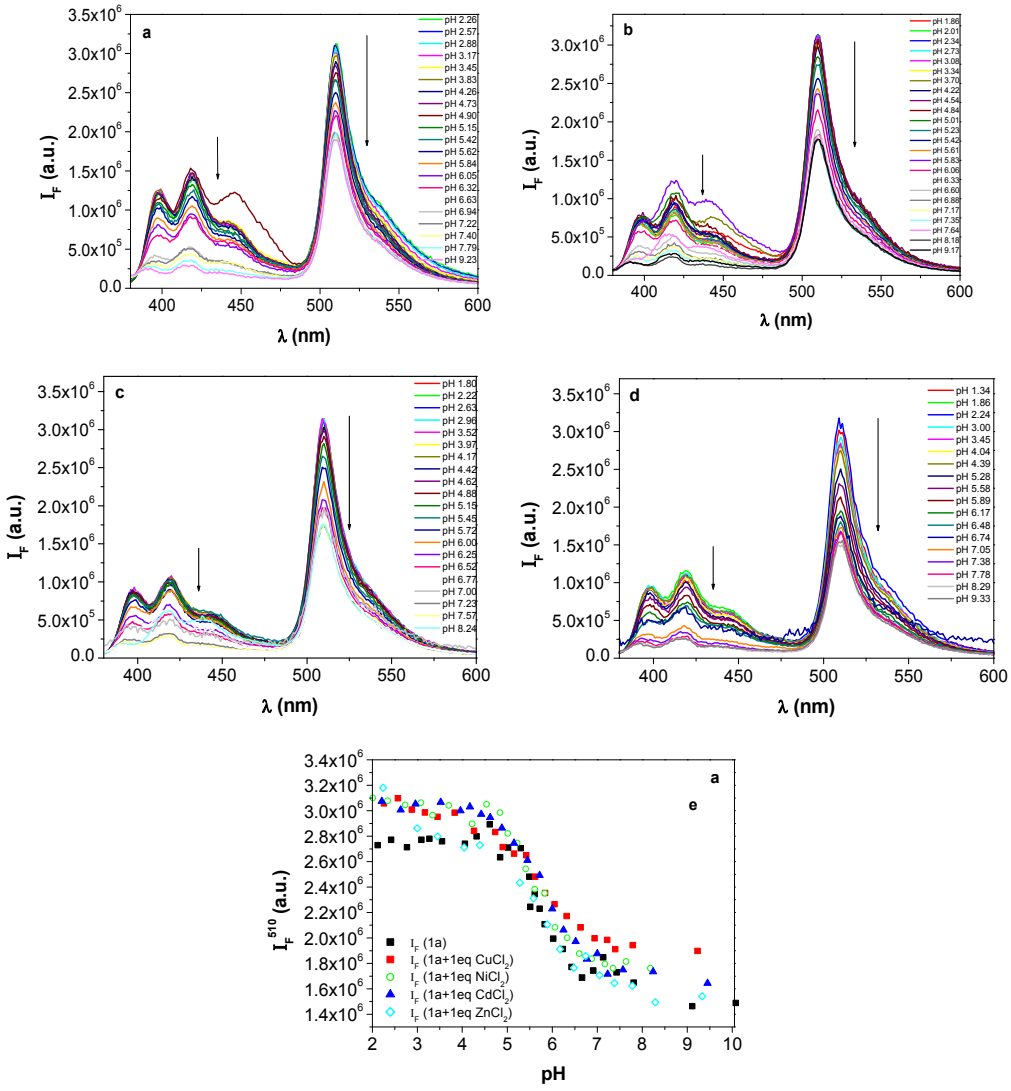

Figure S12. Fluorescence pH titration of compound **1a** in the presence of 1eq of different metallic cations: **a)** Cu, **b)** Ni, **c)** Cd and **d)** Zn. **e)** Comparative graph showing the effect of M^{2+} cations on fluorescence of **1a**.Measurement media: **1a** ($5 \cdot 10^{-6}$ M) + MCl_2 ($5 \cdot 10^{-6}$ M) in PBS 0.1 M buffered aqueous media (1.25% DMSO). λ_{exc}=368 nm.

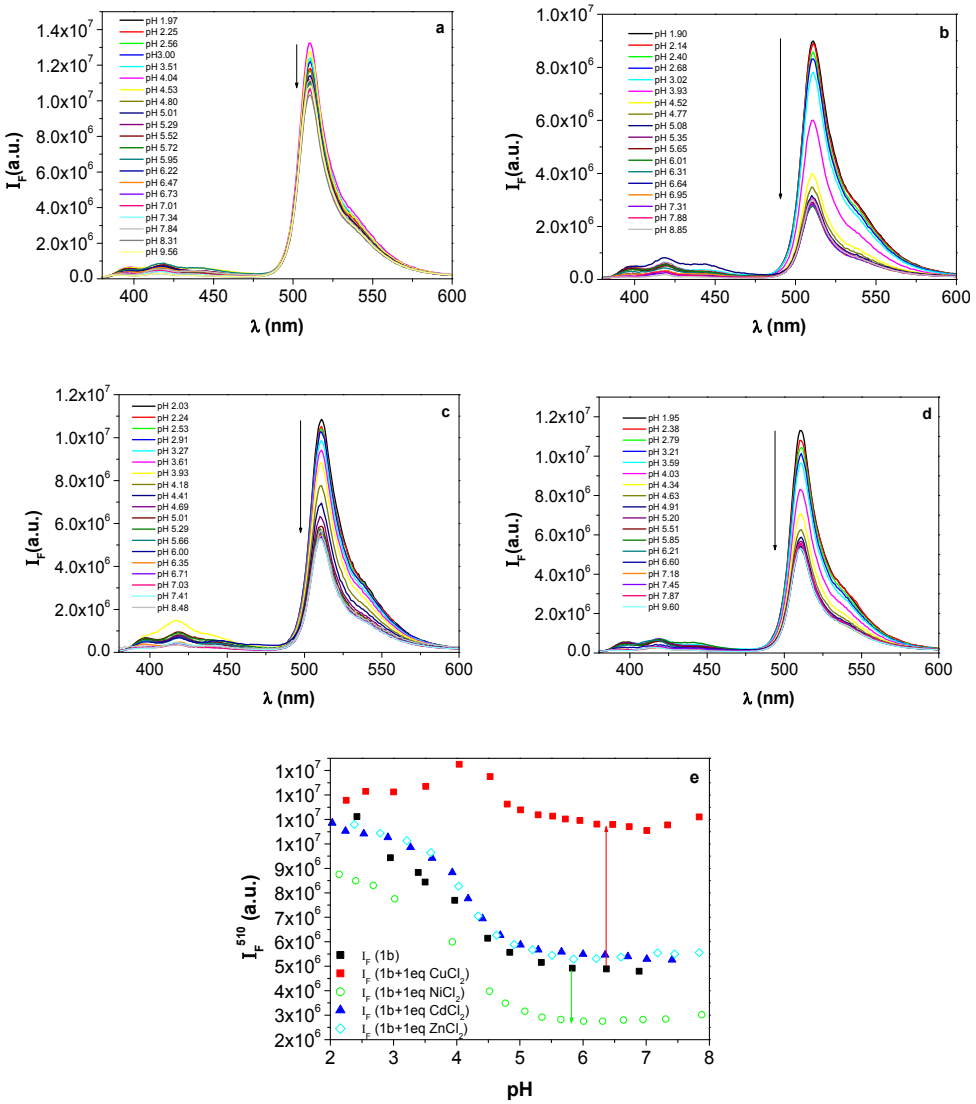

Figure S13. Fluorescence pH titration of compound **1b** in the presence of 1eq of different metallic cations: **a)** Cu, **b)** Ni, **c)** Cd and **d)** Zn. **e)** Comparative graph showing the effect of M^{2+} cations on fluorescence of **1b**. Measurement media: **1b** ($5 \cdot 10^{-6}$ M) + MCl_2 ($5 \cdot 10^{-6}$ M) in PBS 0.1 M buffered aqueous media (1.25% DMSO). λ_{exc}=368 nm.

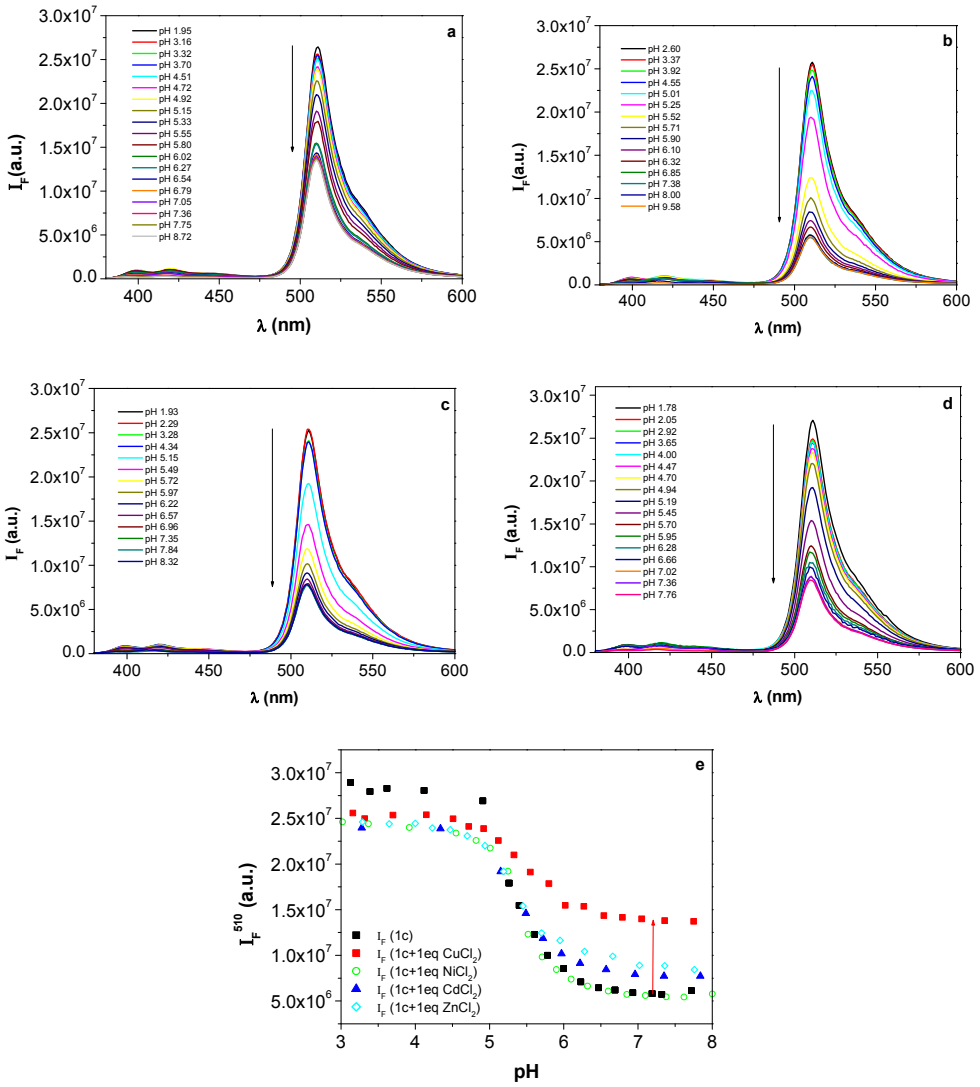

Figure S14. Fluorescence pH titration of compound **1c** in the presence of 1eq of different metallic cations: **a)** Cu, **b)** Ni, **c)** Cd and **d)** Zn. **e)** Comparative graph showing the effect of M^{2+} cations on fluorescence of **1c**. Measurement media: **1c** ($5\cdot10^{-6}$ M) + MCl_2 ($5\cdot10^{-6}$ M) in PBS 0.1 M buffered aqueous media (1.25% DMSO). λ_{exc}=368 nm.

Table S2. Fluorescence emission intensities for the different compounds in presence of 1eq of various metallic cations (aqueous PBS buffered media) and calculated enhancement factors.

	+Metal (I_F)					+Metal (Enhancement factor)			
	without M^{2+}	Cu^{2+}	Ni^{2+}	Cd^{2+}	Zn^{2+}	Cu^{2+}	Ni^{2+}	Cd^{2+}	Zn^{2+}
1a	$1.85\cdot10^6$	$1.99\cdot10^6$	$1.76\cdot10^6$	$1.84\cdot10^6$	$1.71\cdot10^6$	1.1	1.0	1.0	0.9
1b	$4.84\cdot10^6$	$1.05\cdot10^7$	$2.82\cdot10^6$	5.32E·10^6 6	$5.46\cdot10^6$	2.2	0.6	1.1	1.1
1c	$5.91\cdot10^6$	$1.4\cdot10^7$	$5.65\cdot10^6$	$7.92\cdot10^6$	$8.1\cdot10^6$	2.4	1.0	1.3	1.4