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Intermolecular hydrogen bonding assisted aggregation induced emission in quinolone–quinazoline conjugates and their potential use in acidochromism

Irshad Ali,[a+] Bhupendra Kumar Dwivedi,[a,b+] Vishwa Deepak Singh,[a] and Daya Shankar Pandey[a]*

Department of Chemistry, Institute of Science, Banaras Hindu University, Varanasi–221005, India

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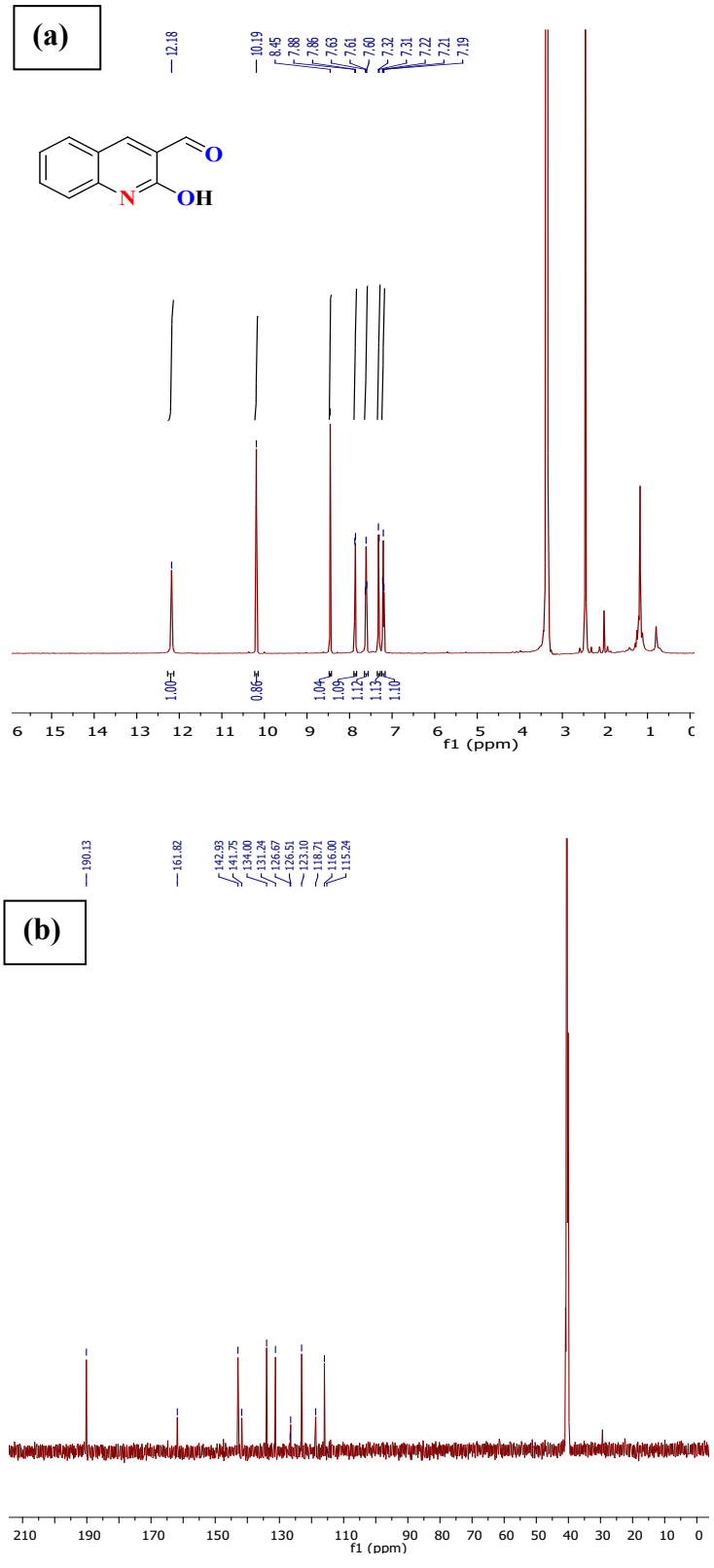
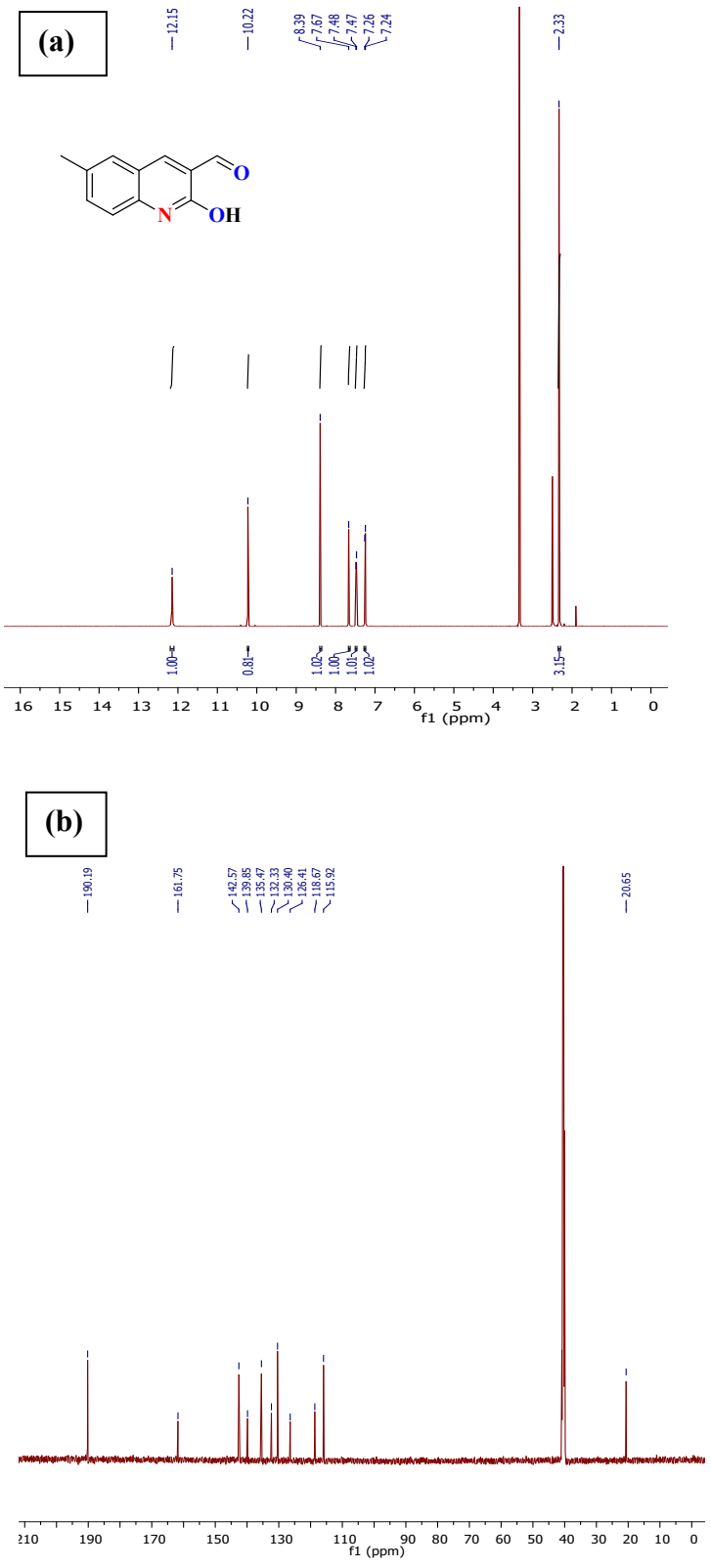


Fig. S1 ^{1}H (a) and ^{13}C (b) NMR spectra of **A1**.



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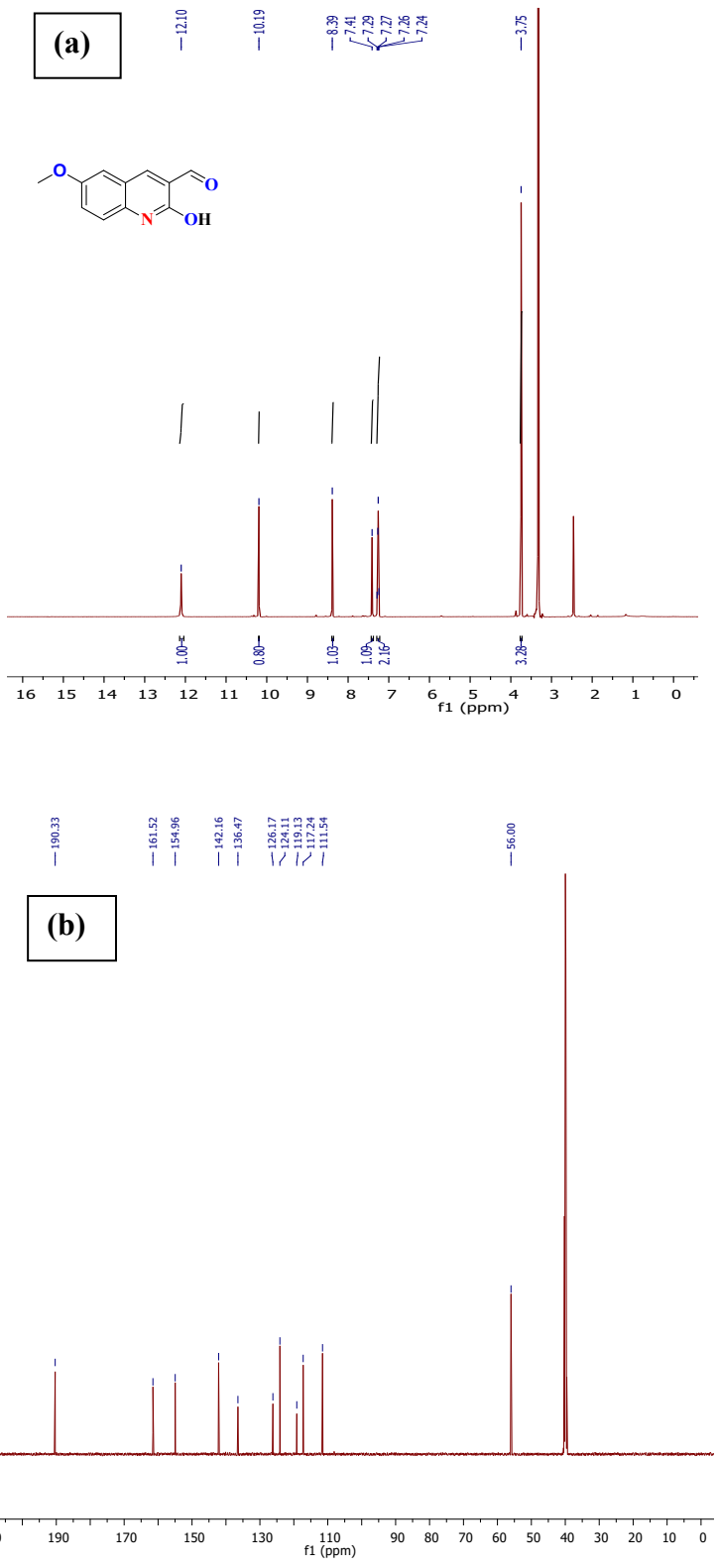

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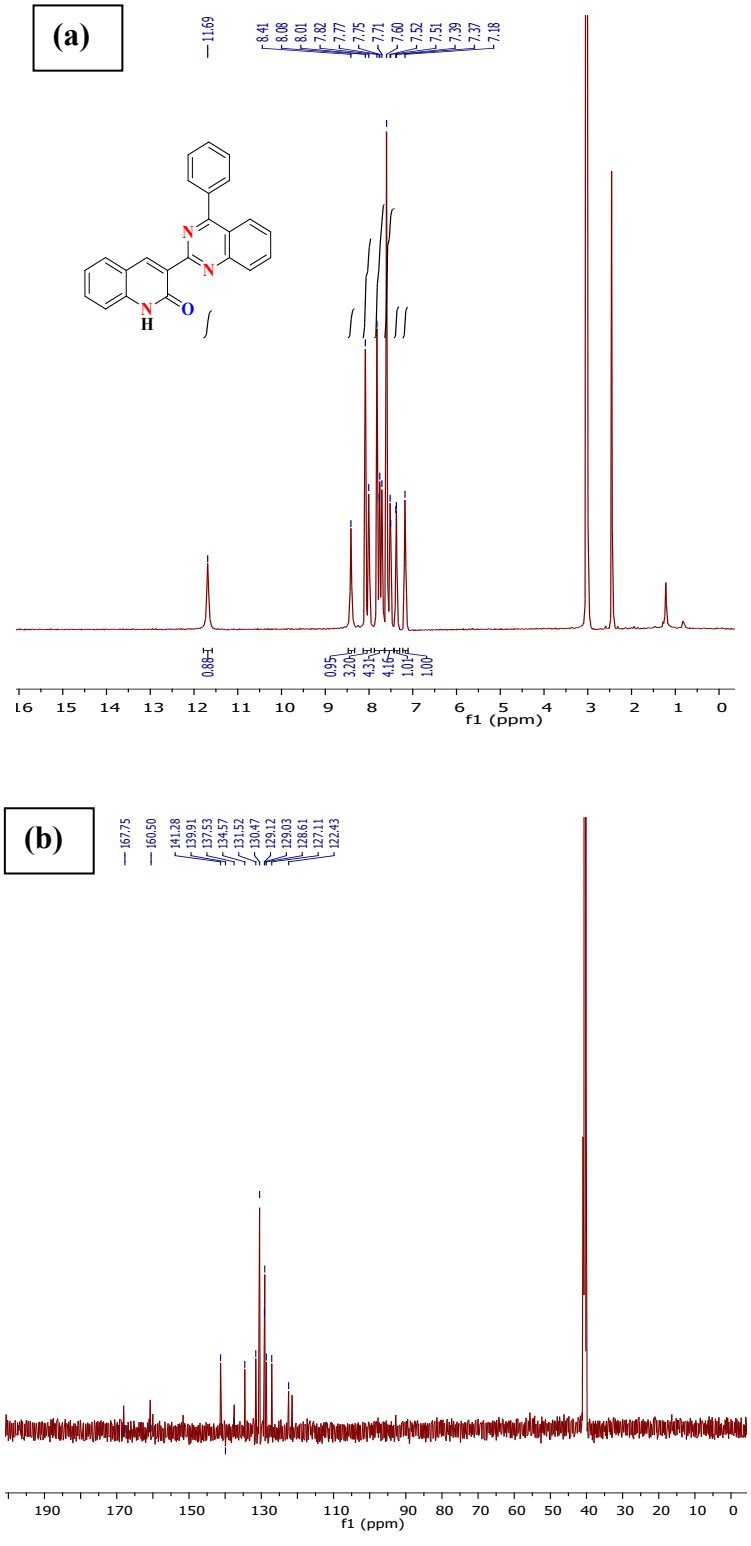

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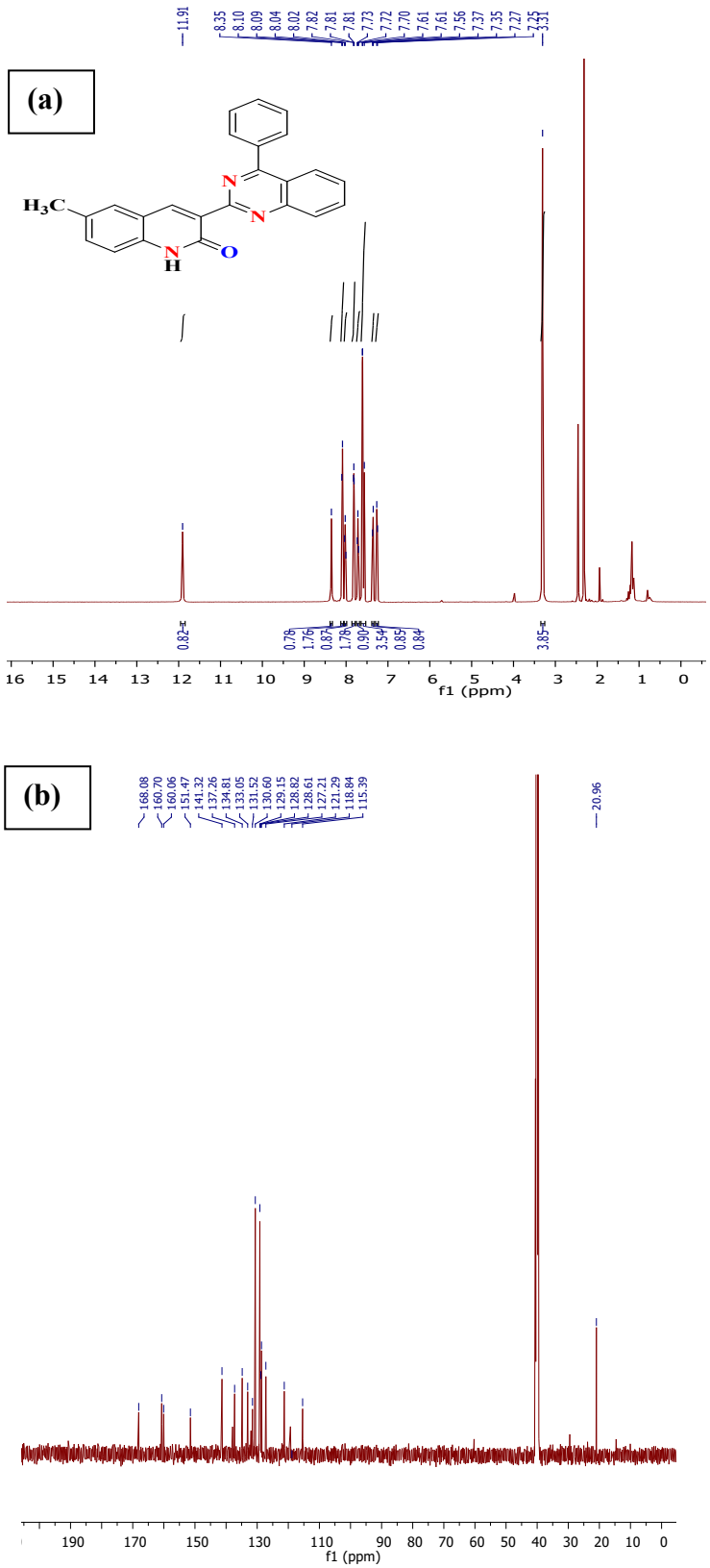

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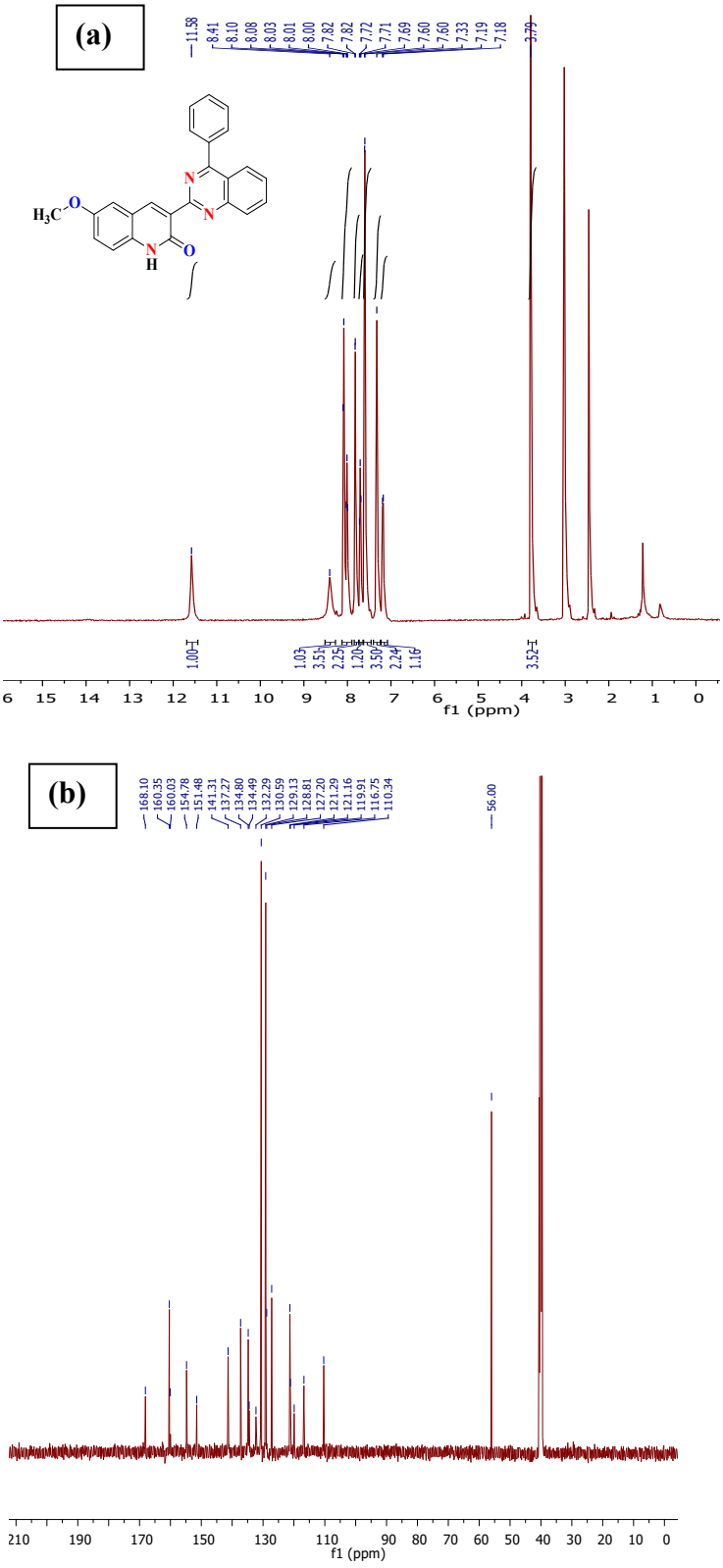

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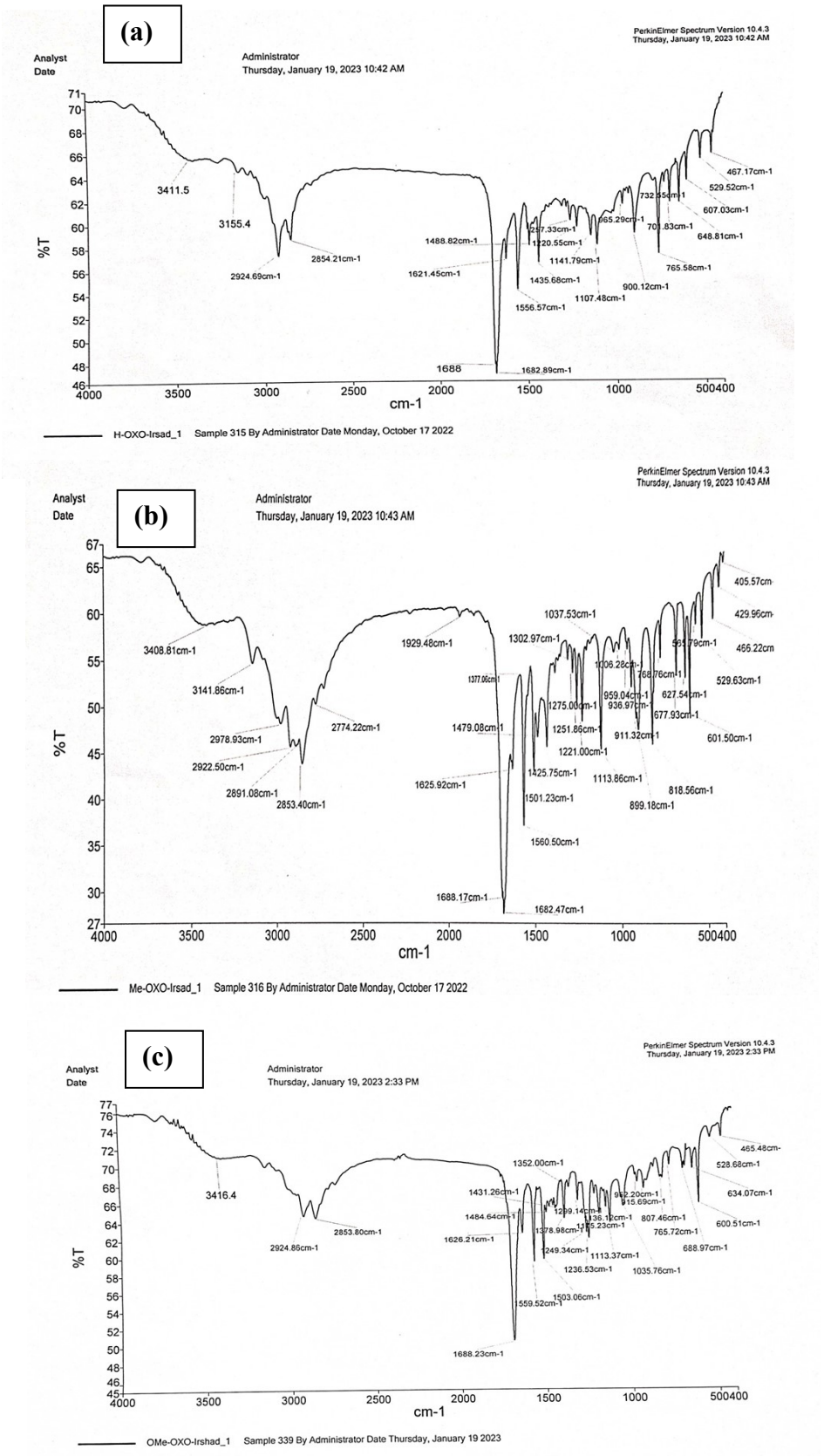

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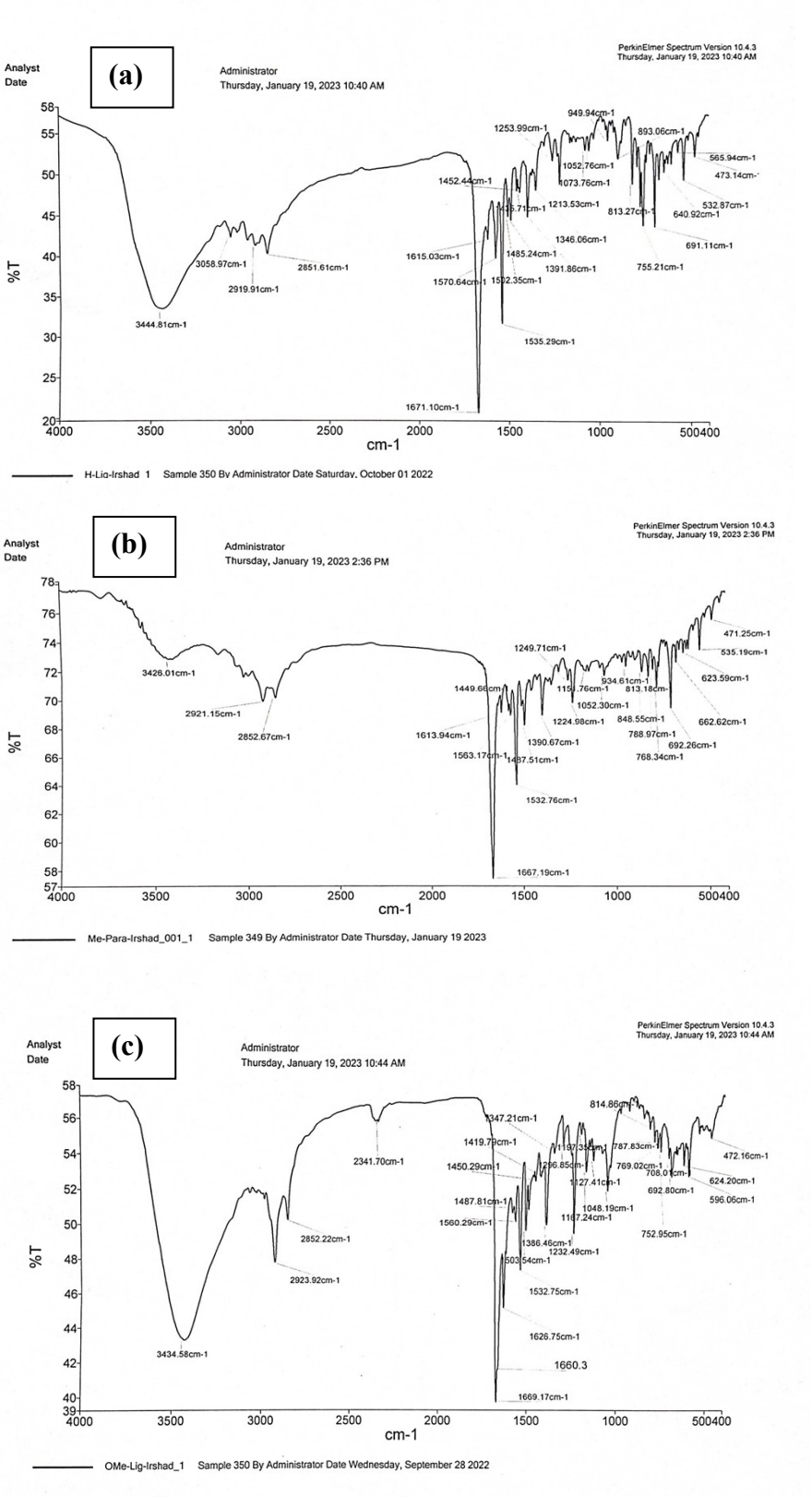

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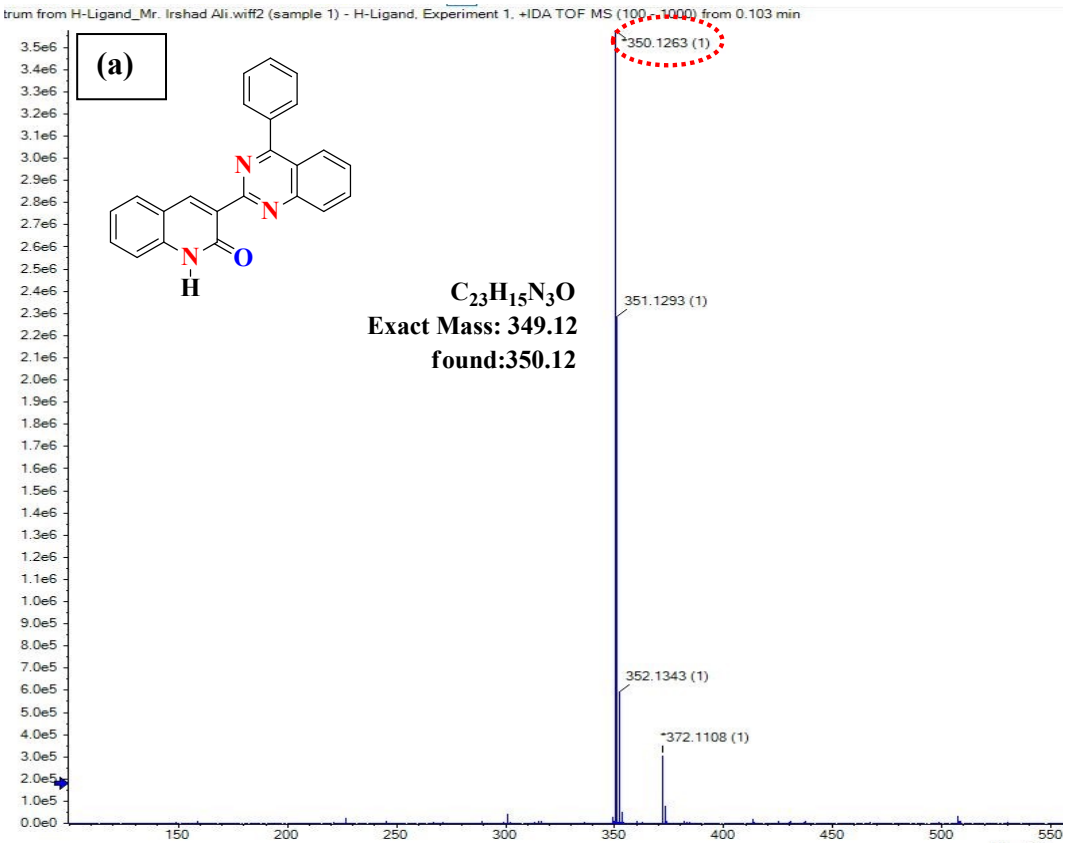

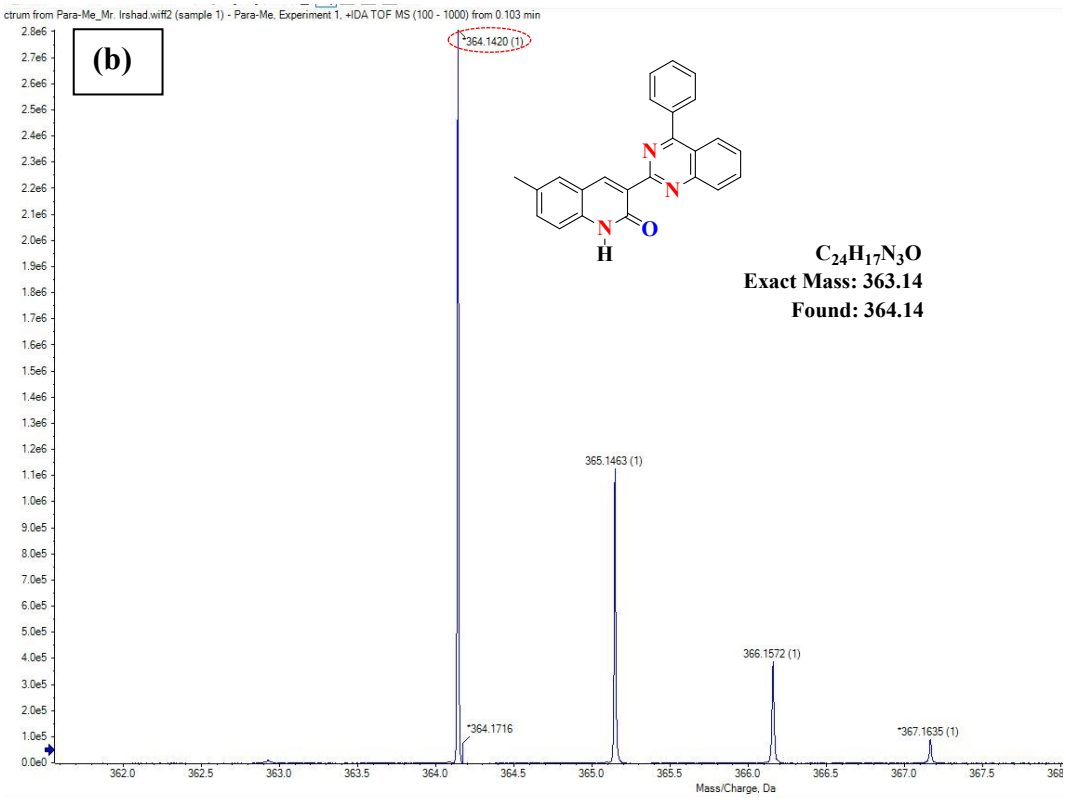

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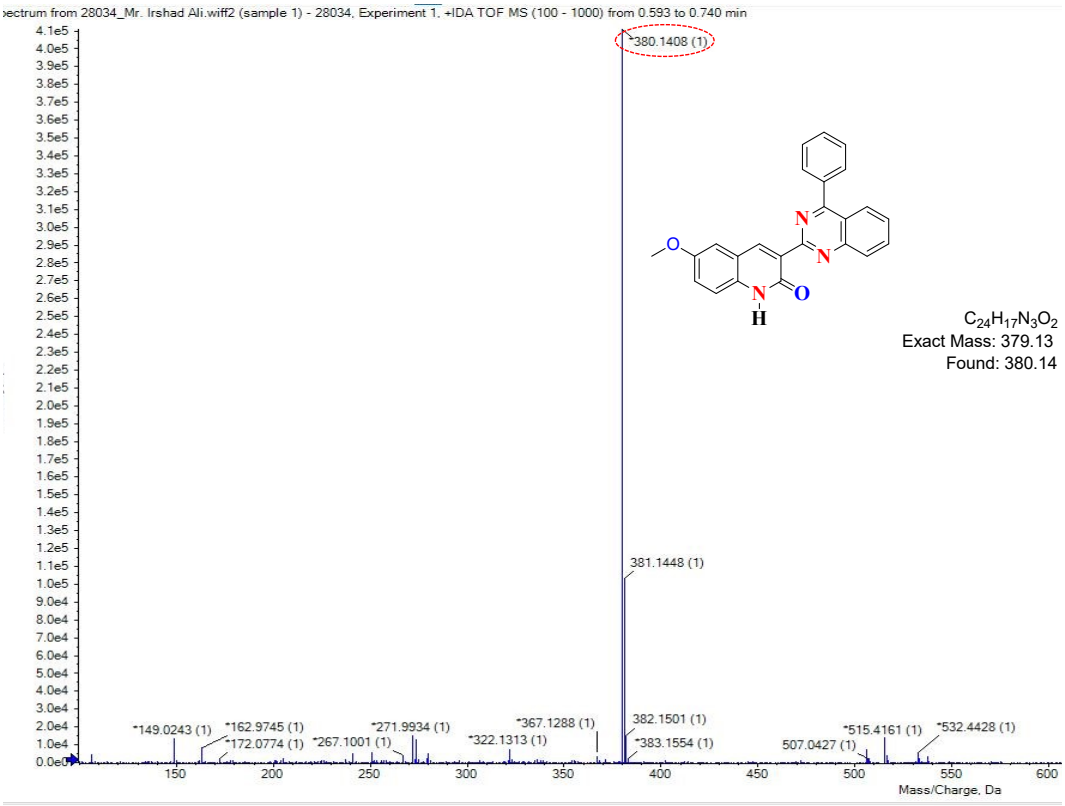

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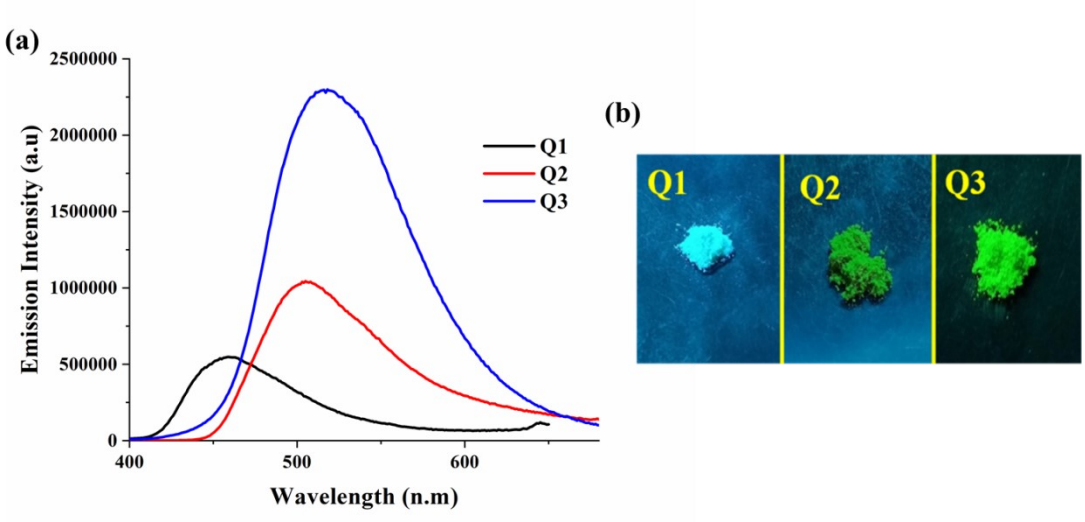

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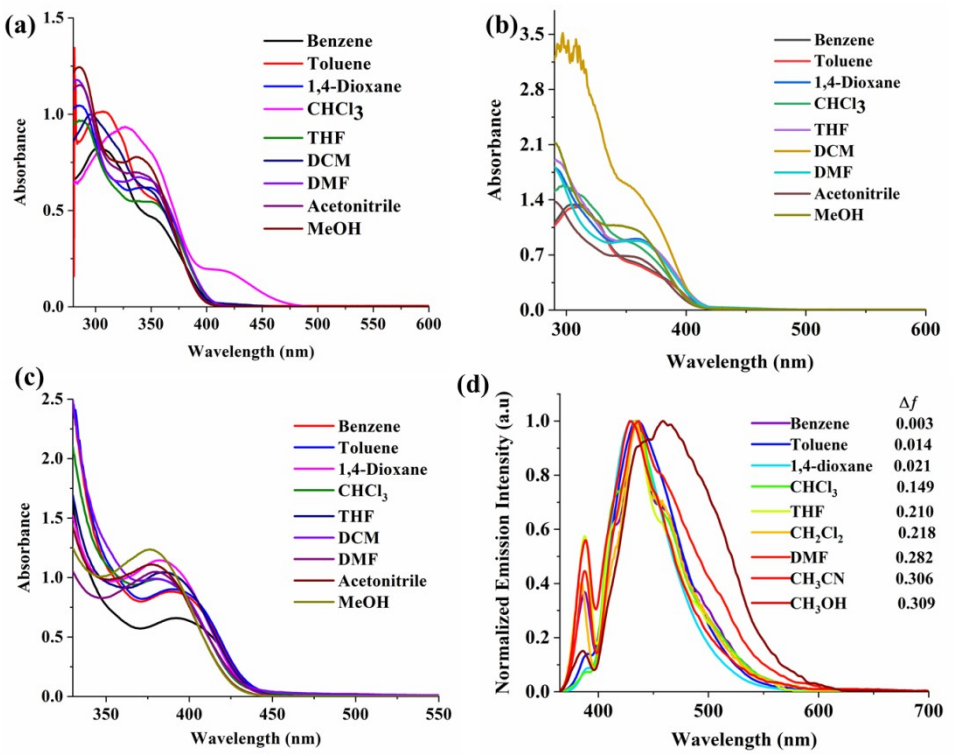

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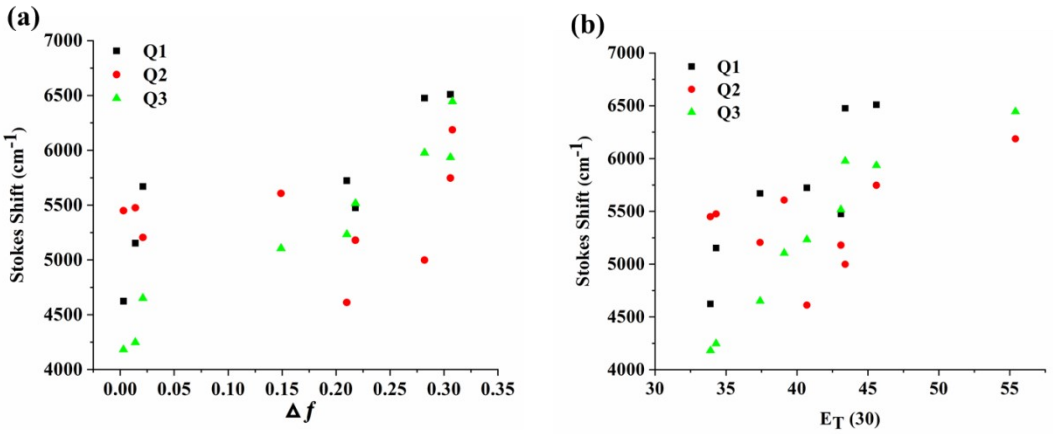

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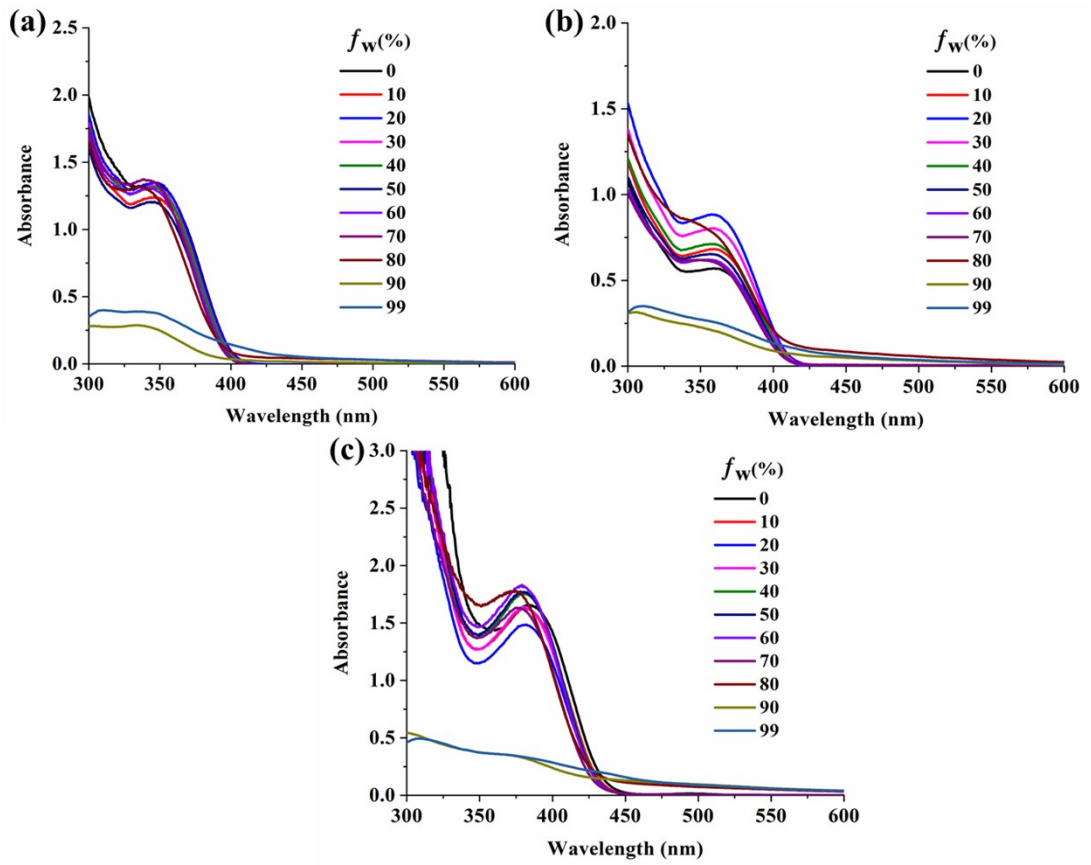

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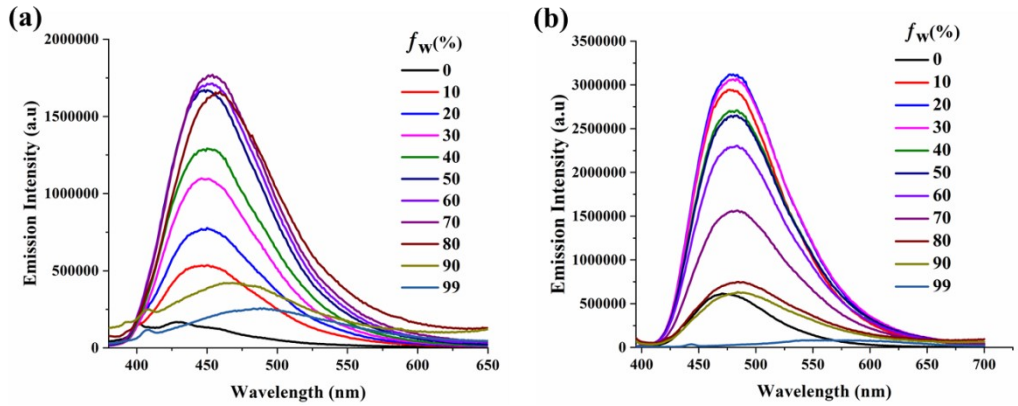

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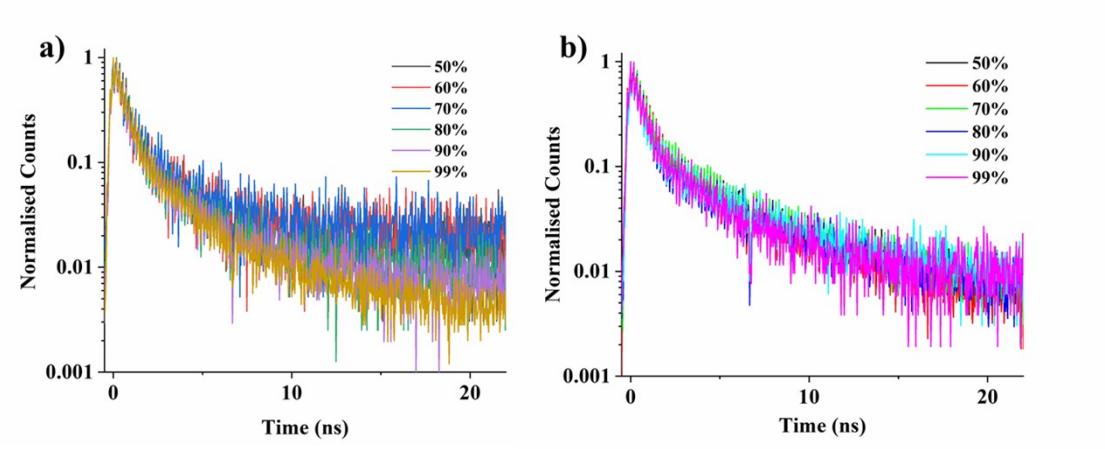

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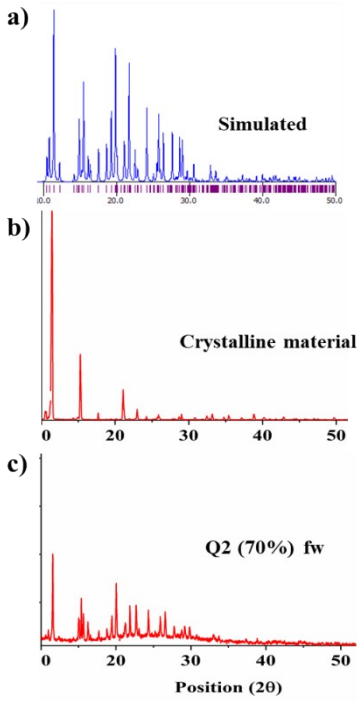

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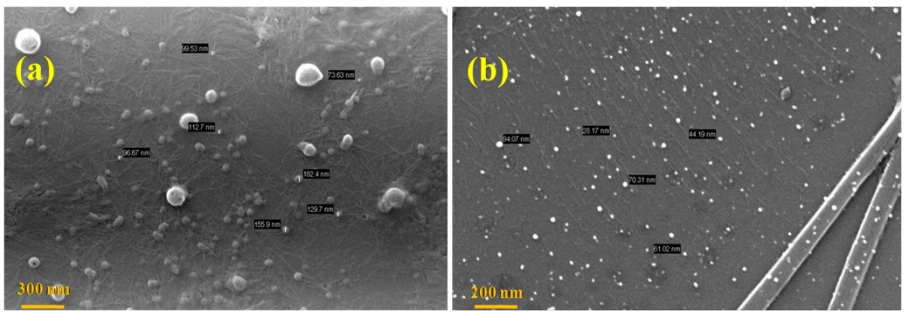

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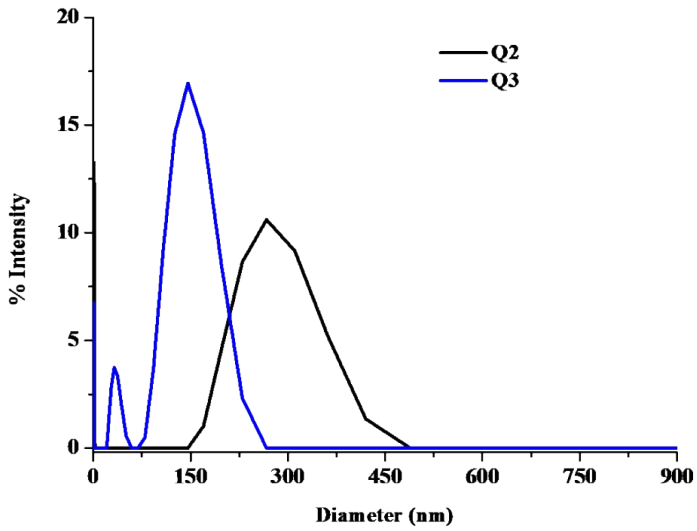

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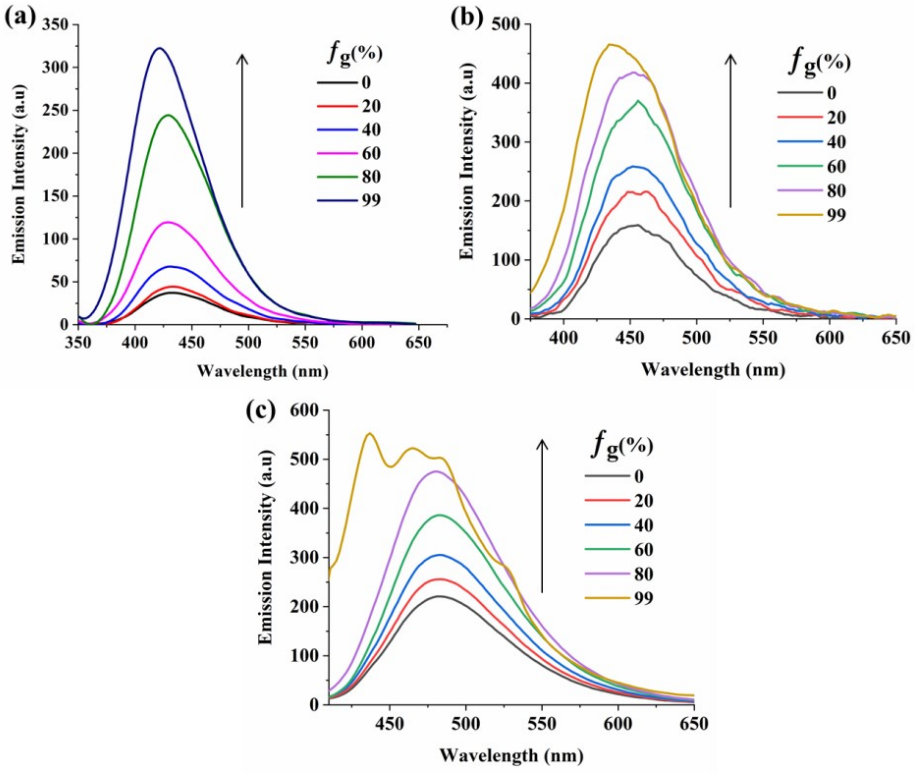

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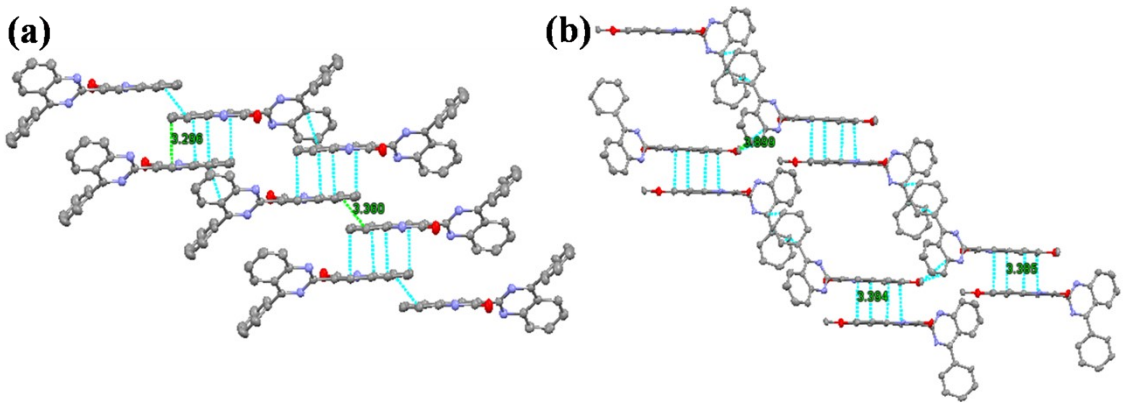


Fig. S21 Crystal packing of **Q1** (a), and **Q3** (b) through π–π stacking.

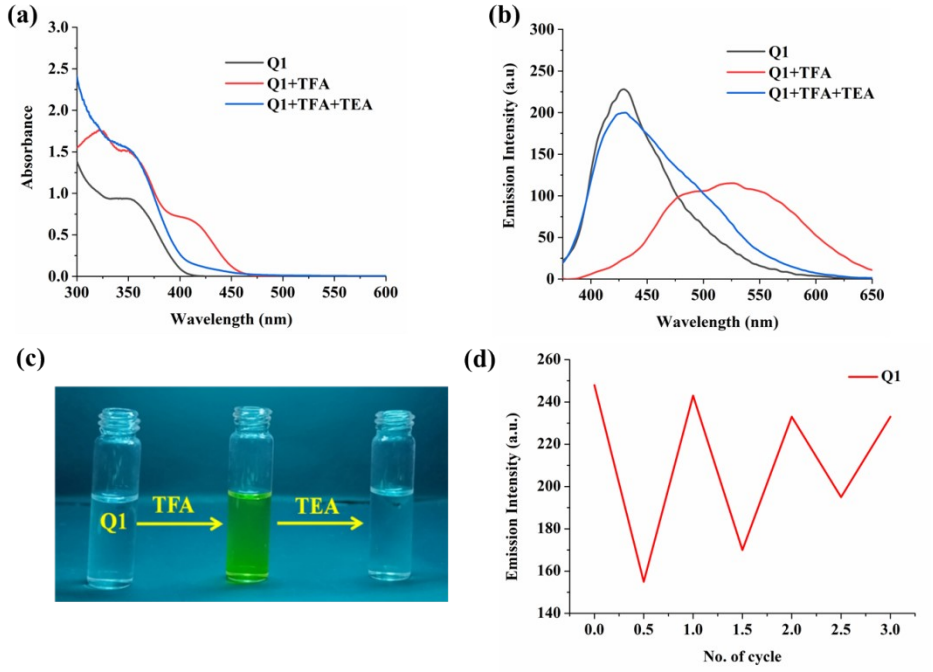
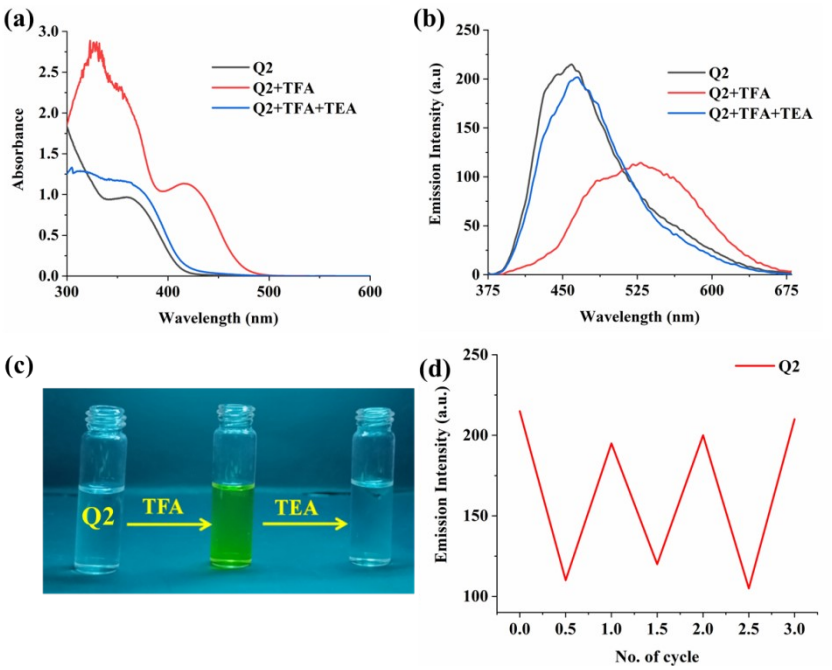


Fig. S22 (a) Absorption spectrum of **Q1**, **Q1**+**TFA** and **Q1**+**TFA**+**TEA**. (b) Emission spectrum of **Q1**, **Q1**+**TFA** and **Q1**+**TFA**+**TEA**. (c) Images of **Q1** ($c=5\times10^{-5}$ $molL^{-1}$) showing emission color changes after the addition of TFA and TEA, under the UV radiation of 365 nm. (d) Reversible switching of the emission of **Q1** by TFA/TEA cycle.



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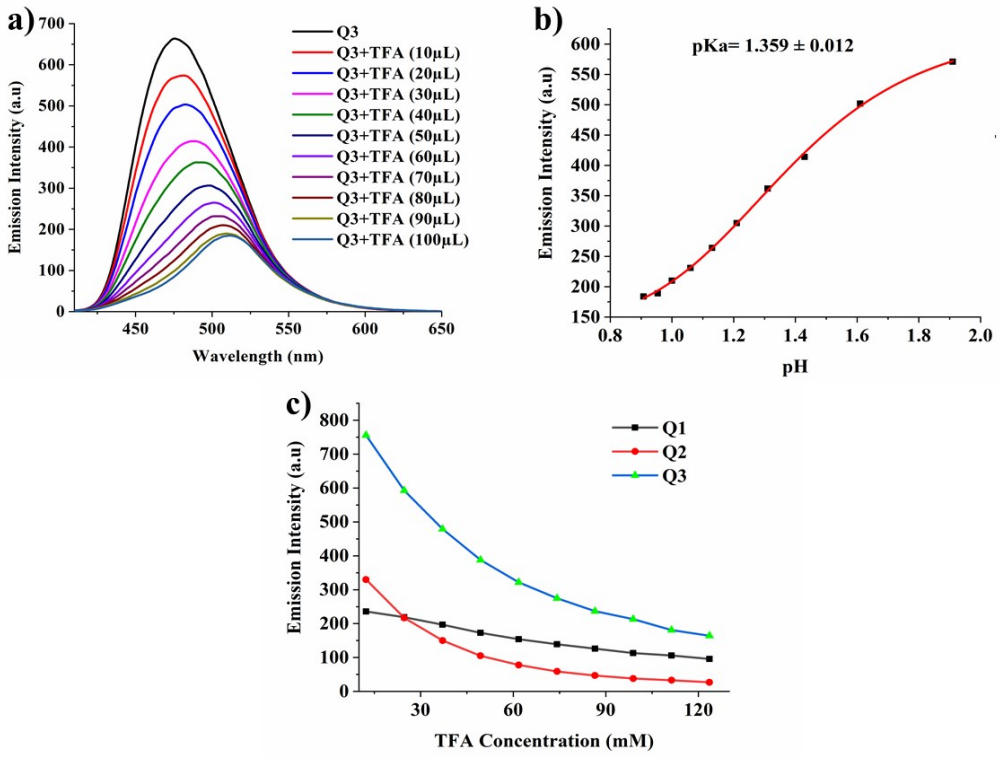

Fig. S24 (a) Emission spectrum of **Q3**, with addition of TFA (10-100 µL) **Q3+TFA** (b) calculation of pKa by performing pH dependent fluorescence titration of Q3 in THF (c; 50 µM) at different pH (1.91, 1.61, 1.43, 1.31, 1.21, 1.13, 1.06, 1, 0.95, 0.90) (c) quantitative relationship between TFA concentration and emission intensity of Q1, Q2, and Q3.

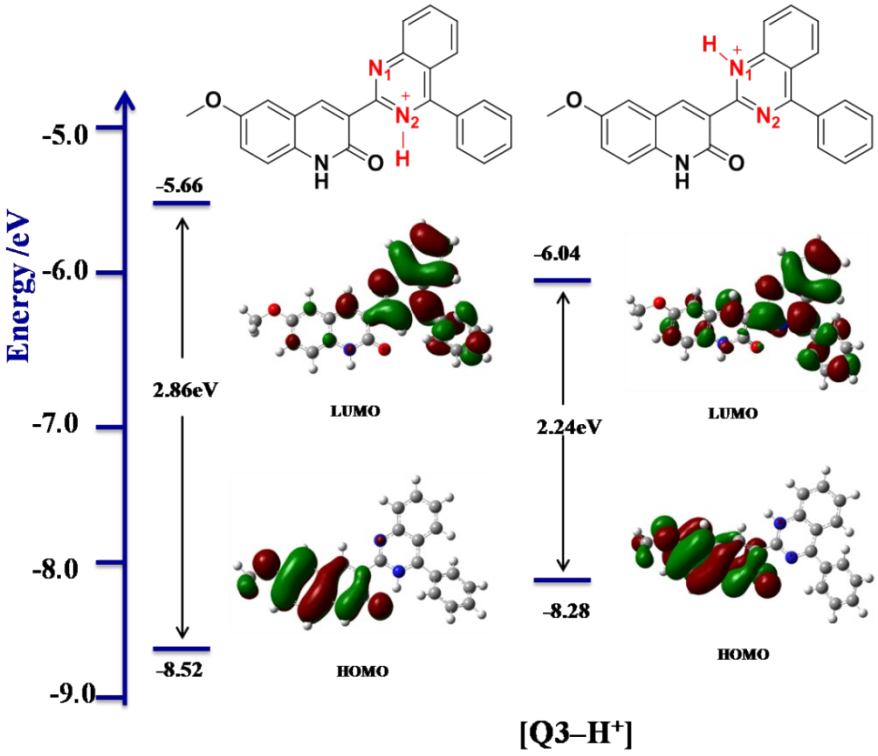

Fig. S25 DFT optimized structure of **[Q3–H⁺].**

Table S1 Selected bond distances in **Q1**, **Q2** and **Q3**.

Q1	Bond Length (Å)	Q2	Bond Length (Å)	Q3	Bond Length (Å)
O1-C23	1.2363(15)	**O1-C10**	1.243(2)	**O4-C10**	1.237(8)
N1-C7	1.3189(16)	**N2-C11**	1.363(2)	**O2-C34**	1.245(9)
N1-C14	1.3613(16)	**N2-C14**	1.325(2)	**O1-C26**	1.371(9)
N2-C14	1.3140(16)	**N1-C5**	1.383(2)	**O1-C25**	1.387(9)
N2-C13	1.3726(16)	**N1-C10**	1.364(2)	**O3-C2**	1.356(10)
N3-C23	1.3635(16)	**N3-C11**	1.311(2)	**O3-C1**	1.414(8)
N3-C22	1.3806(17)	**N3-C12**	1.365(2)	**N4-C29**	1.390(9)
C7-C8	1.4249(18)	**C11-C9**	1.493(2)	**N4-C34**	1.366(8)

C7-C6	1.4875(17)	**C9-C8**	1.347(2)	**N1-C10**	1.356(8)
C8-C13	1.4098(18)	**C9-C10**	1.456(3)	**N1-C7**	1.404(9)
C8-C9	1.4147(18)	**C5-C6**	1.401(3)	**N6-C35**	1.366(9)
C17-C16	1.4292(17)	**C5-C4**	1.387(2)	**N6-C42**	1.335(9)
C17-C22	1.3981(18)	**C6-C8**	1.426(3)	**N5-C35**	1.301(9)
C17-C18	1.4042(18)	**C6-C7**	1.403(2)	**N5-C36**	1.355(9)
C14-C15	1.4809(17)	**C14-C13**	1.427(3)	**N3-C11**	1.374(9)
C15-C23	1.4668(17)	**C14-C15**	1.482(3)	**N3-C18**	1.317(9)
C15-C16	1.3525(17)	**C13-C12**	1.417(3)	**N2-C11**	1.292(8)
C6-C1	1.3861(19)	**C13-C21**	1.414(3)	**N2-C12**	1.388(8)
C6-C5	1.376(2)	**C15-C16**	1.398(3)	**C35-C33**	1.490(9)

Table S2 Selected bond angles in **Q1**, **Q2** and **Q3**.

Q1	**Bond angle (°)**	**Q2**	**Bond angle (°)**	**Q3**	**Bond angle (°)**
C14-N1-C7	117.84(11)	**C14-N2-C11**	117.68(16)	**C1-O3-C2**	117.6(6)
C13-N2-C14	116.29(11)	**C10-N1-C5**	125.33(18)	**C7-N1-C10**	125.0(6)
C22-N3-C23	125.56(12)	**C12-N3-C11**	116.17(16)	**C18-N3-C11**	118.3(6)
C8-C7-N1	121.52(12)	**N3-C11-N2**	126.92(17)	**C12-N2-C11**	117.3(6)
C6-C7-N1	115.14(11)	**C9-C11-N2**	114.84(16)	**N2-C11-N3**	125.8(6)
C6-C7-C8	123.05(11)	**C9-C11-N3**	118.17(16)	**C9-C11-N3**	114.5(6)
C13-C8-C7	115.93(11)	**C8-C9-C11**	120.37(16)	**C9-C11-N2**	119.7(6)
C9-C8-C7	124.80(12)	**C10-C9-C11**	118.78(17)	**C12-C17-C18**	116.7(7)
C9-C8-C13	119.00(12)	**C10-C9-C8**	120.84(17)	**C16-C17-C18**	125.5(7)
C22-C17-C16	117.60(11)	**C6-C5-N1**	119.12(17)	**C16-C17-C12**	117.7(7)
C18-C17-C16	123.72(12)	**C4-C5-N1**	121.25(17)	**N1-C10-O4**	121.4(7)
C18-C17-C22	118.64(12)	**C4-C5-C6**	119.62(18)	**C9-C10-O4**	122.7(6)
N2-C14-N1	126.49(12)	**C8-C6-C5**	117.24(17)	**C9-C10-N1**	115.9(6)
C15-C14-N1	116.16(11)	**C7-C6-C5**	118.78(18)	**C4-C7-N1**	120.5(7)
C15-C14-N2	117.34(11)	**C7-C6-C8**	123.98(18)	**C6-C7-N1**	118.6(6)
C23-C15-C14	118.39(11)	**C13-C14-N2**	120.96(17)	**C6-C7-C4**	120.8(7)

C16-C15-C14	121.63(11)	**C15-C14-N2**	115.93(16)	**C10-C9-C11**	119.2(6)
C16-C15-C23	119.84(12)	**C15-C14-C13**	123.10(17)	**C8-C9-C11**	120.0(7)
N3-C23-O1	120.28(12)	**C6-C8-C9**	122.23(18)	**C8-C9-C10**	120.7(6)
C15-C23-O1	124.23(12)	**C12-C13-C14**	116.06(17)	**C3-C4-C7**	119.5(7)
C15-C23-N3	115.46(11)	**C21-C13-C14**	125.26(17)	**C8-C6-C7**	117.6(7)
C1-C6-C7	117.20(12)	**C21-C13-C12**	118.62(17)	**C5-C6-C7**	118.4(7)
C5-C6-C7	123.66(13)	**N1-C10-O1**	120.80(18)	**C5-C6-C8**	124.0(7)
C5-C6-C1	119.14(13)	**C9-C10-O1**	124.02(18)	**C2-C3-C4**	121.0(7)
C15-C16-C17	122.51(12)	**C9-C10-N1**	115.17(18)	**C17-C18-N3**	120.9(7)
C17-C22-N3	118.89(12)	**C16-C15-C14**	118.77(17)	**C19-C18-N3**	115.2(6)
C21-C22-N3	120.68(12)	**C20-C15-C14**	122.87(18)	**C19-C18-C17**	123.9(7)
C21-C22-C17	120.41(12)	**C20-C15-C16**	118.27(17)	**C6-C8-C9**	122.2(7)
C8-C13-N2	121.87(11)	**C13-C12-N3**	121.98(17)	**C20-C19-C18**	122.6(7)
C12-C13-N2	118.81(12)	**C24-C12-N3**	118.70(18)	**C24-C19-C18**	117.5(7)
C12-C13-C8	119.17(12)	**C24-C12-C13**	119.27(19)	**C24-C19-C20**	119.8(7)

Table S3 Molar extinction coefficient (ε) for **Q1, Q2**, and **Q3** (c; 50 μM)

Compounds	**Absorption maxima**	**Molar extinction Coefficient (ε)**
Q1	337	2.40 X 10^5 M^{-1} cm^{-1}
Q2	358	2.35 X 10^5 M^{-1} cm^{-1}
Q3	385	2.09 X 10^5 M^{-1} cm^{-1}

Table S4 Emission maxima (λ_{em}) in the solid-state for **Q1, Q2**, and **Q3.**

Compounds	**Emission maxima (THF solution)**	**Emission maxima (Solid state)**
Q1	433	459
Q2	440	505
Q3	463	518

Table S5 Absorption and emissions maxima for **Q1, Q2**, and **Q3** in THF/water mixtures.

Water (vol %)	Q1		Q2		Q3	
	λ_{ab}/nm	λ_{em}/nm	λ_{ab}/nm	λ_{em}/nm	λ_{ab}/nm	λ_{em}/nm
0	337	401	358	429	385	465
10 to 80	346	438	355	450	382	483
90	306-333	480	303-358	462	285-298	488
99	309-337	499	311-358	490	286-305	-----

Table S6 Fluorescence quantum yield (Φ_f) for **Q1** at different water fractions (f_w) in THF/water mixtures.

Water fraction (vol %)	Fluorescence quantum yield (Φ_f) Q1
0%-40%	0.005
50%-60%	0.010
70%	0.013
80%	0.022
90%	0.191
99%	0.073

Fluorescence quantum yield (Φ_F) for **Q1** have beencalculated relative to quinine sulphate (THF, λex = 310 nm, λem = 358 nm, Φ = 0.55) as a reference using the formula $[(\Phi F = \Phi_R \times (I_T/I_R) \times (A_R/A_T) \times (\eta T^2/\eta R^2)]$, where Φ = quantum yield, I = area under the curve of emission spectrum, A = absorbance at λex, η = refractive index of solvent; The subscript R and T denote values for the reference and test samples respectively. Stock solutions for **Q1** have been prepared in THF; error ±5%.

Table S7 Average life time ($\tau_{avg.}$) for **Q1** at water fractions (f_w) from 50%-99% in THF/water mixtures.

Q1 (Water vol %)	τ1 (ns)	τ2 (ns)	A1	A2	$\tau_{avg.}$	R^2
50	0.272	2.328	0.685	0.091	0.515	0.888

60	0.446	2.918	0.724	0.060	0.546	0.917
70	0.444	2.210	0.702	0.074	0.612	0.935
80	0.433	2.479	0.617	0.149	0.751	0.914
90	0.811	2.315	0.629	0.219	1.199	0.923
99	0.607	2.168	0.689	0.189	0.943	0.927

Table S8 Average life time ($\tau_{avg.}$) for **Q2** at water fractions (f_w) from 50%-99% in THF/water mixtures.

Q2 (Water vol %)	**τ1 (ns)**	**τ2 (ns)**	**A1**	**A2**	**$\tau_{avg.}$**	**R^2**
50	0.437	2.789	0.671	0.092	0.722	0.902
60	0.499	3.246	0.736	0.073	0.748	0.935
70	0.413	2.360	0.609	0.132	0.871	0.907
80	0.399	2.609	0.596	0.101	0.720	0.918
90	0.468	2.925	0.727	0.078	0.708	0.924
99	0.336	1.854	0.550	0.163	0.684	0.889

Table S9 Average life time ($\tau_{avg.}$) for **Q3** at water fractions (f_w) from 50%-99% in THF/water mixtures.

Q3 (Water vol %)	**τ1 (ns)**	**τ2 (ns)**	**A1**	**A2**	**$\tau_{avg.}$**	**R^2**
50	0.515	3.95	0.668	0.118	1.033	0.924
60	0.487	4.135	0.713	0.104	0.953	0.928
70	0.428	2.586	0.560	0.150	0.885	0.926
80	0.341	2.803	0.533	0.132	0.830	0.911
90	0.478	2.829	0.651	0.113	0.822	0.920
99	0.361	3.066	0.585	0.115	0.806	0.919