Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplimentary Information

The Nature of Binding of Quinolate Complex on the Surface of ZnS Quantum Dot

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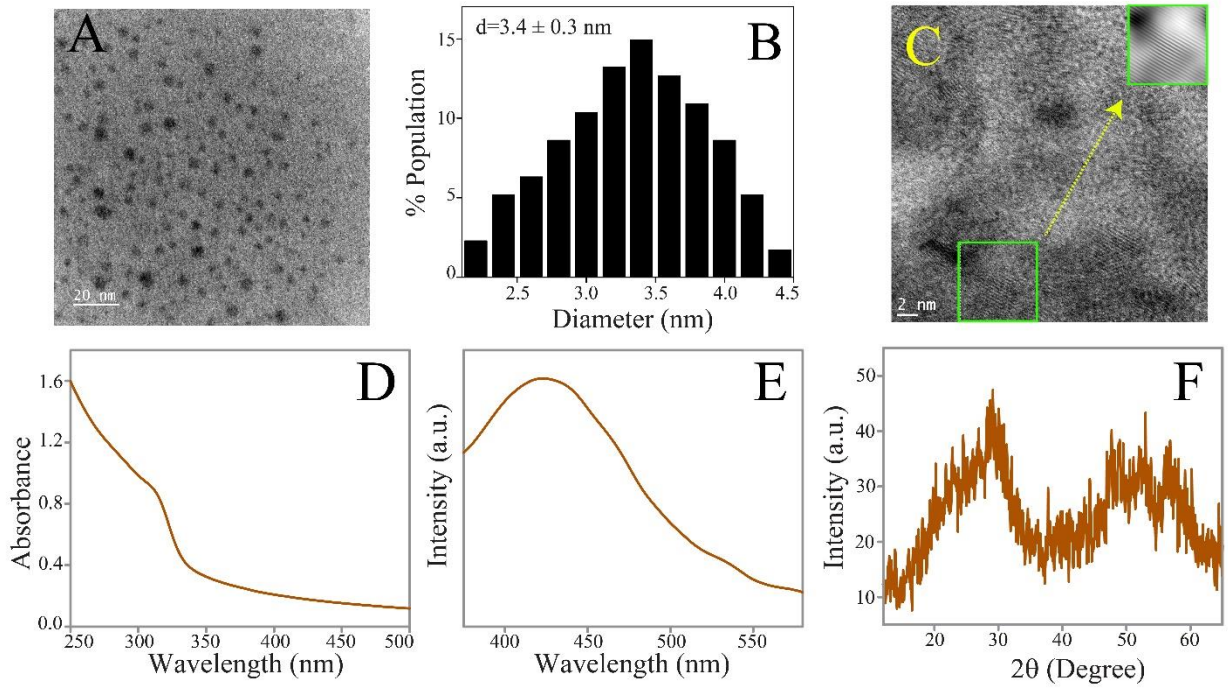

Figure S1. (A) Transmission electron microscopic (TEM) image, (B) corresponding particle size distribution, (C) high resolution TEM image, (D) UV-vis spectrum, (E) photoluminescence emission spectrum (λ_{ex} – 325 nm) (aqueous dispersion) and (F) powder XRD pattern of as-synthesized ZnS quantum dots.

Formation of wurtzite phase is more favourable over cubic phase when ethylene diamine is used in reaction medium and which acts as capping ligand. The characteristics peaks at 2θ = 26.9º, 29.0º, 32.9º, 41.0, 47.8º, 53.0º and 57.0º due to (100), (002), (101), (102), (110), (103), and (112) planes depicts the wurtzite phase of ZnS.[1]

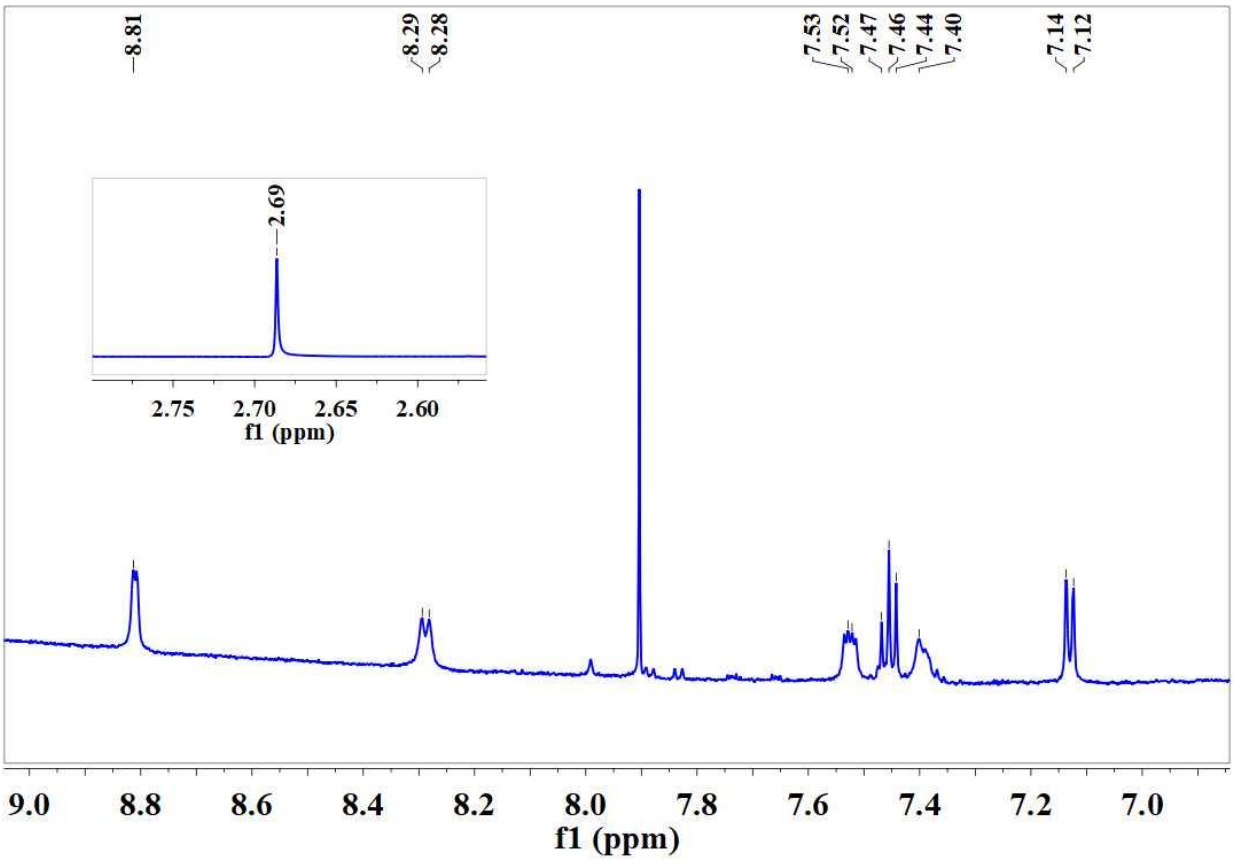

Figure S2. Proton NMR spectrum of reaction mixture consisting of 30.0 μL 50.0 mM HQ and ZnS Qdot in methanol-d_4. (inset) NMR spectrum of DMSO used as internal standard.

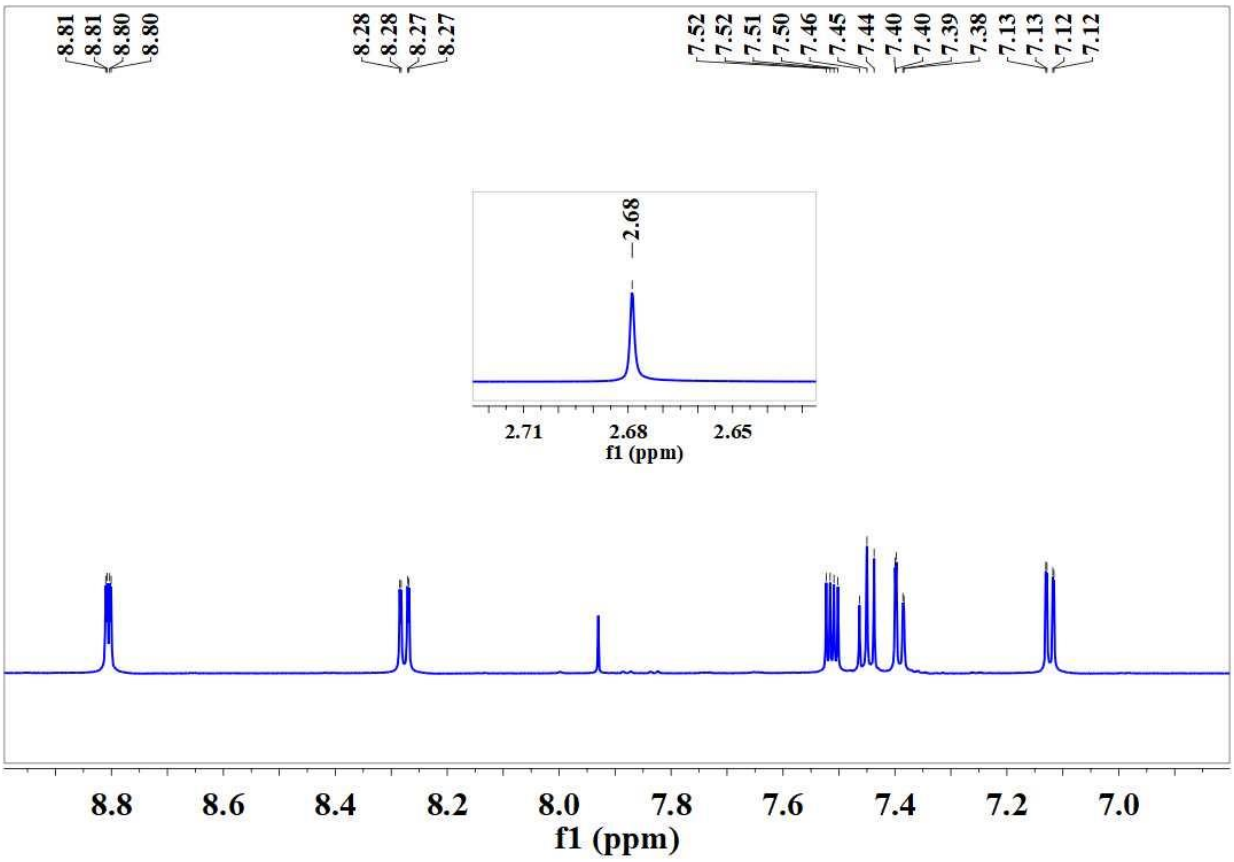

Figure S3. Proton NMR spectrum of reaction of 10 μL 50 mM HQ and ZnS Qdot in methanol-d_4. (inset) NMR spectrum of DMSO used as internal standard.

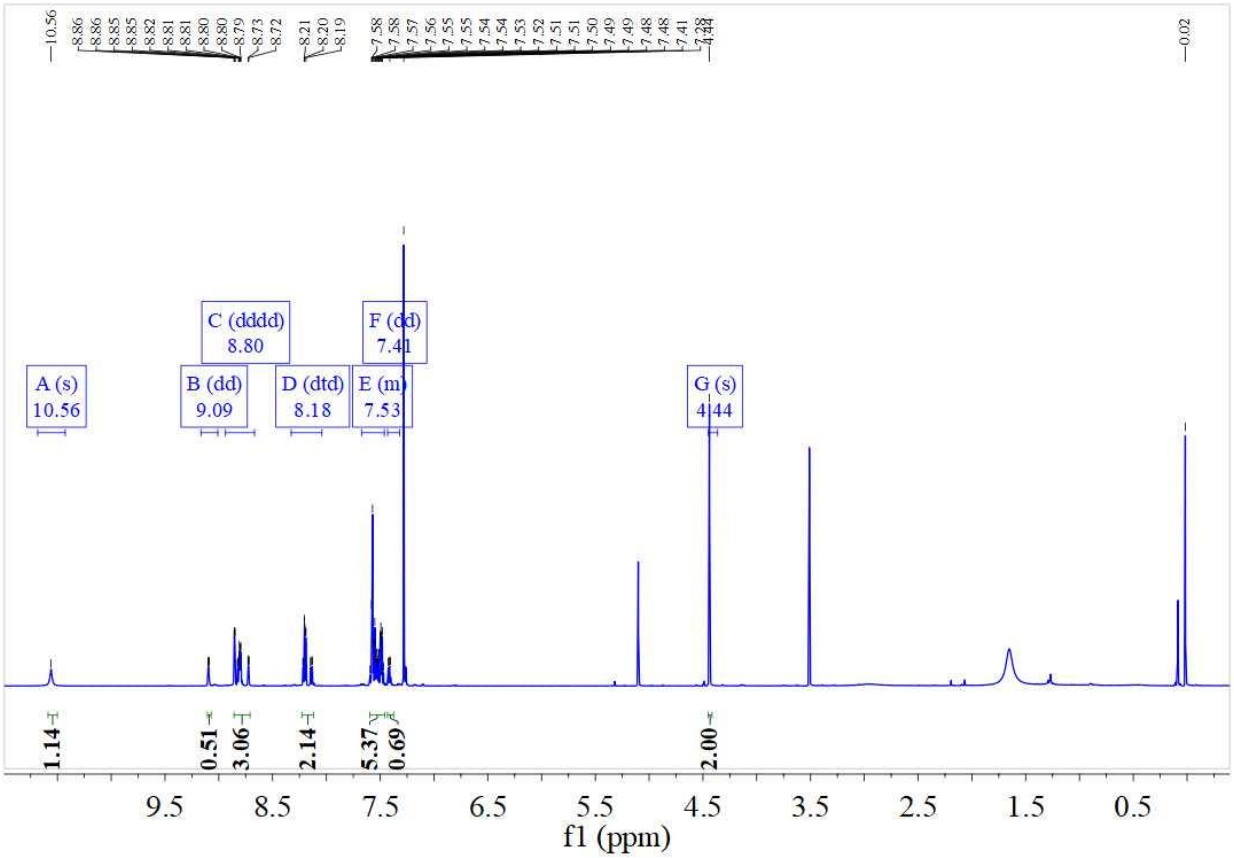

Figure S4. Proton NMR spectrum of N-(quinolin-8-yl)-2-(quinolin-8-yloxy)acetamide (L1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.56 (s, 1H), 9.09 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.80 (dddd, *J* = 48.2, 45.0, 4.2, 1.6 Hz, 2H), 8.18 (dtd, *J* = 9.8, 8.0, 1.6 Hz, 2H), 7.67 – 7.46 (m, 3H), 7.41 (dd, *J* = 8.3, 4.2 Hz, 1H), 4.44 (s, 1H).

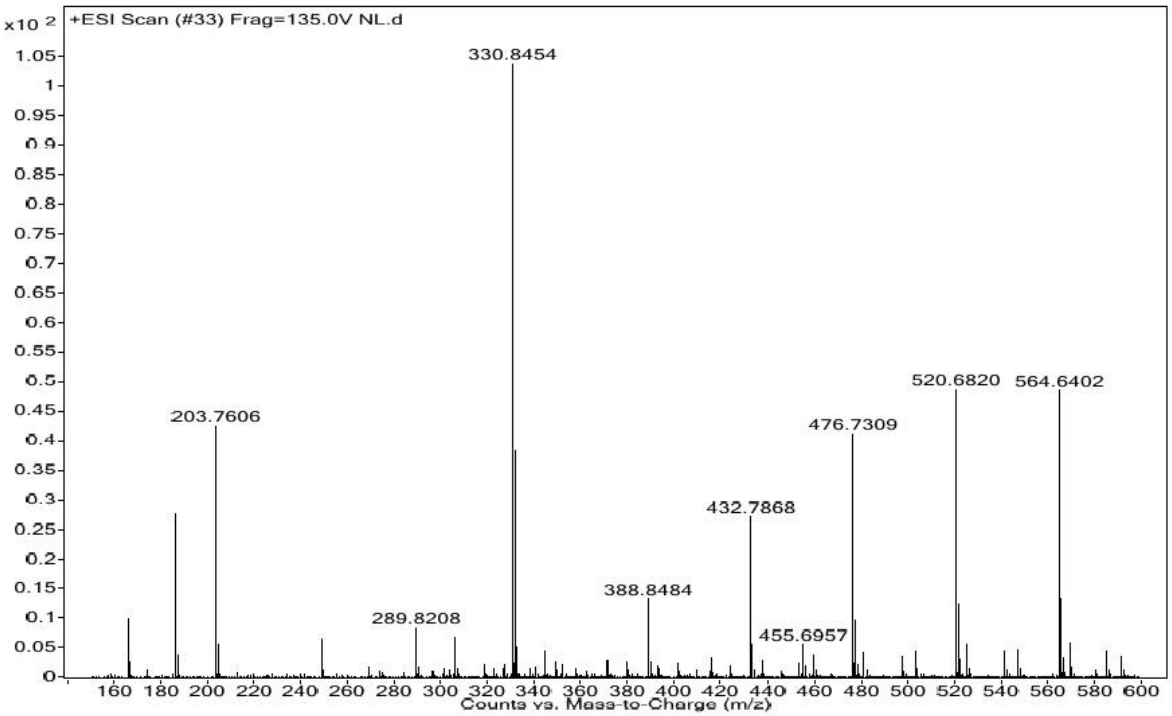

Figure S5. ESI-MS spectrum of L1.

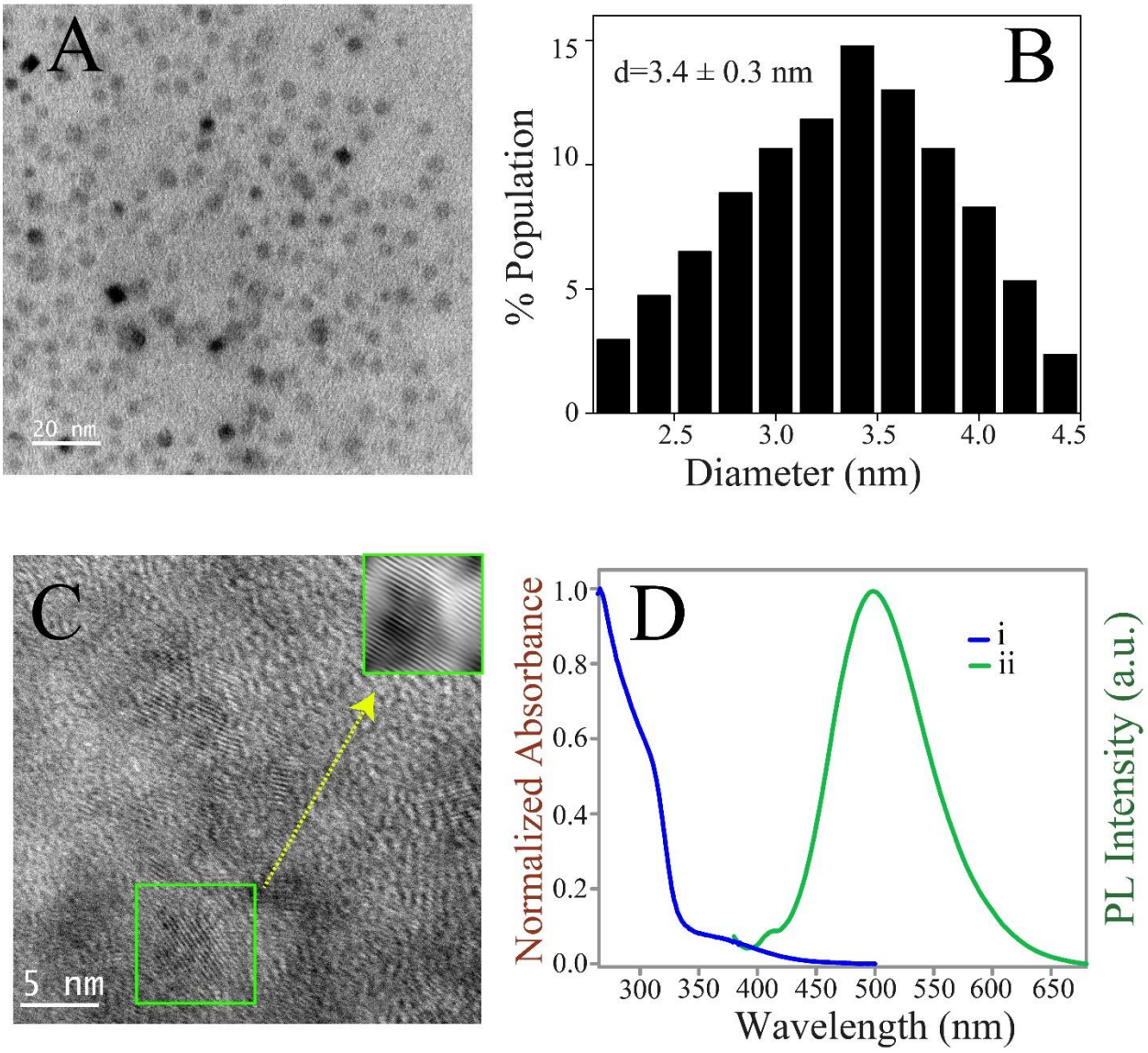

Figure S6. (A) Transmission electron microscopic (TEM) image (scale bar- 10 nm) and (B) corresponding particle size distribution, (C) high resolution TEM image (scale bar - 5 nm) and corresponding inverse fast Fourier transform (IFFT) image (inset) and (D) UV-vis and emission spectrum (λ_{ex}-365 nm) of QDC (in DMSO).

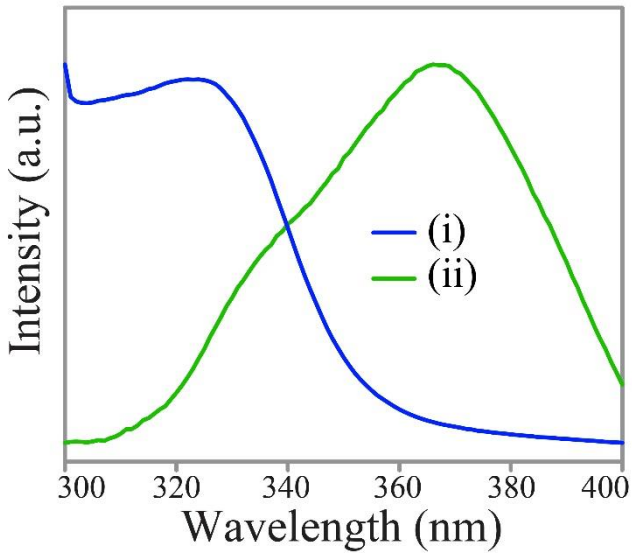

Figure S7. Photoluminescence excitation spectra of (i) as synthesized ZnS Qdots (λ_{em}= 440 nm) in aqueous solution and (ii) QDC (λ_{em}= 500 nm) in DMSO.

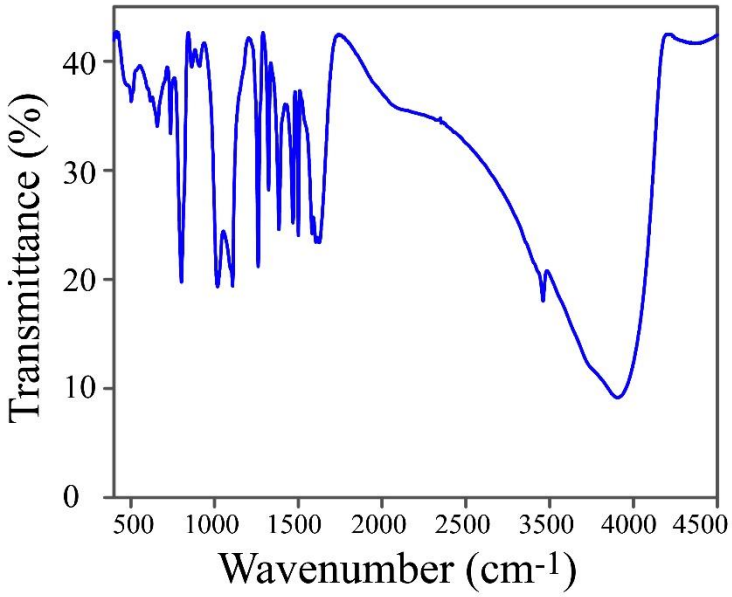

Figure S8. Fourier transform infrared (FTIR) spectrum of the solid sample (KBr pellet) of ZnS-Q QDC.

Table S1. FTIR peak assignment corresponding to Fig S8.[1-2]

FTIR peak (wavenumber, cm^{-1})	Band assignment (functional group)
1604	C–N/ C–C stretching
1582	C–N/ C–C stretching
1500	C–H bending of pyridyl ring
1468	C–H bending of pyridyl ring
1322	C–H bending of pyridyl ring
1108	Zn–O–C– stretching
820	C–H wagging (out of plane)
803	C–H wagging (out of plane)
737	Ring deformation (in plane), C–H wagging (out of plane)
655	Ring deformation (in plane)
615	Ring deformation (in plane)

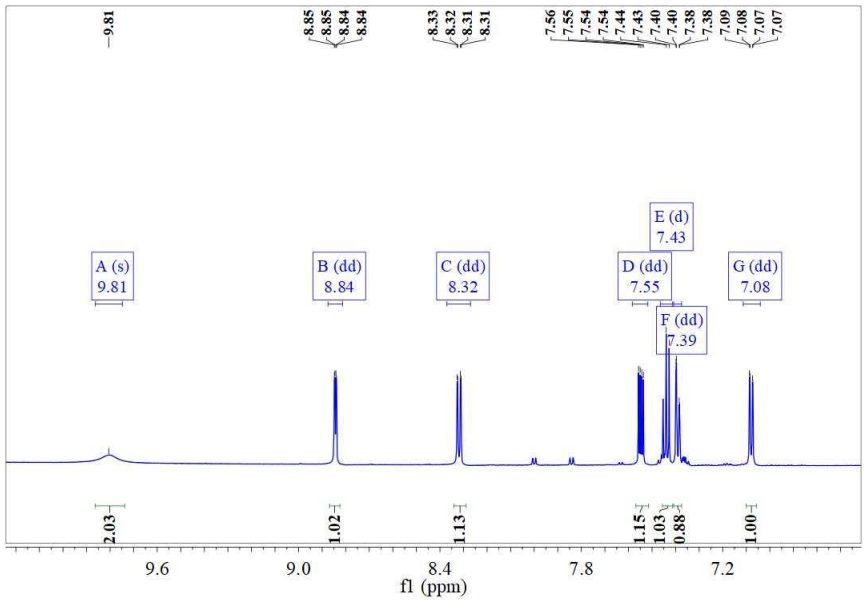

Figure S9. Proton NMR spectrum of 8-hydroxyquinoline (HQ). ^{1}H NMR (600 MHz, DMSO) δ 9.81 (s, 1H), 8.84 (dd, *J* = 4.1, 1.6 Hz, 1H), 8.32 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.55 (dd, *J* = 8.3, 4.1 Hz, 1H), 7.43 (d, *J* = 7.6 Hz, 1H), 7.39 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.08 (dd, *J* = 7.5, 1.3 Hz, 1H).

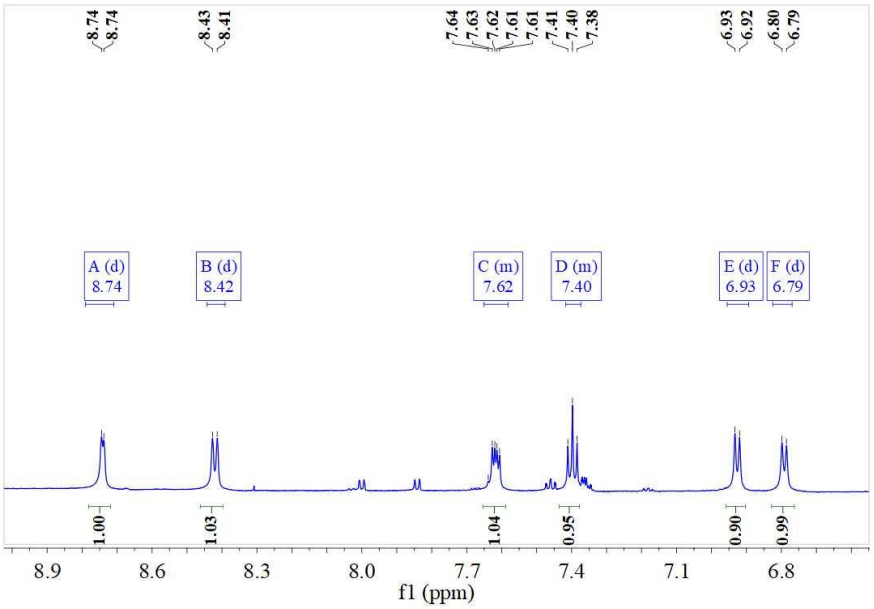

Figure S10. Proton NMR spectrum of ZnQ_2. ^{1}H NMR (600 MHz, DMSO) δ 8.74 (d, *J* = 3.7 Hz, 1H), 8.42 (d, *J* = 8.1 Hz, 1H), 7.65 – 7.58 (m, 1H), 7.42 – 7.37 (m, 1H), 6.93 (d, *J* = 7.9 Hz, 1H), 6.79 (d, *J* = 7.7 Hz, 1H).

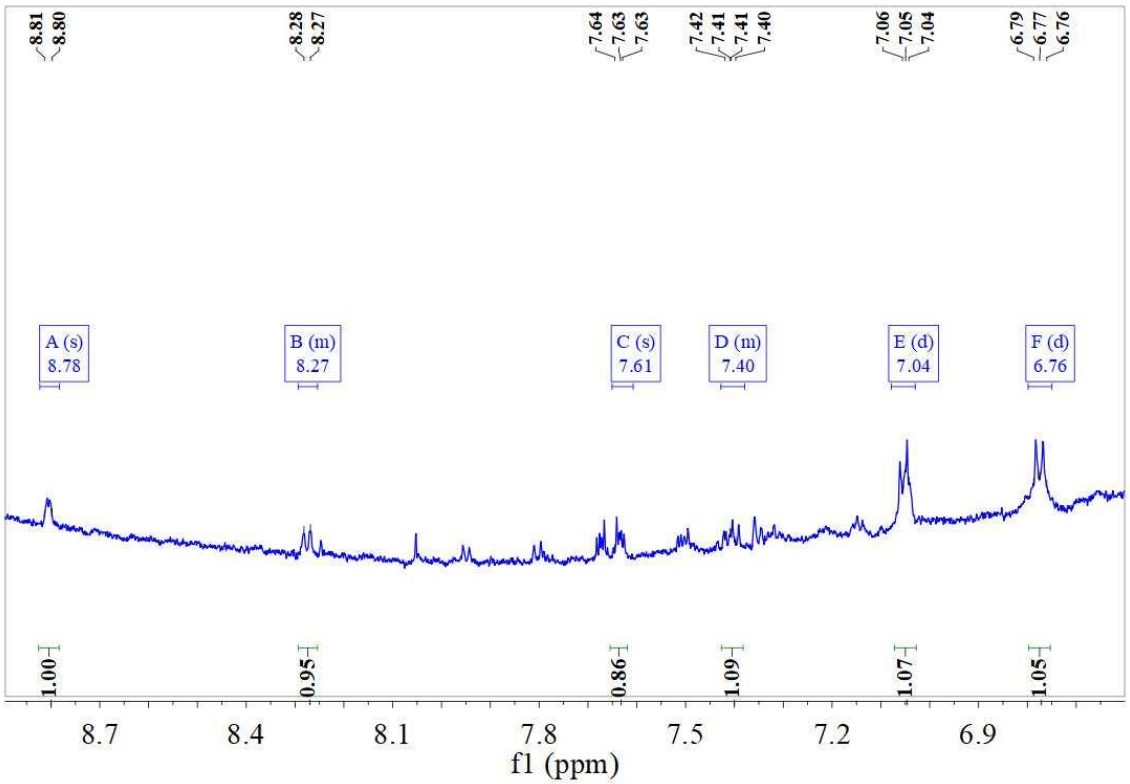

Figure S11. Proton NMR spectrum of supernatant obtained after centrifugation of as prepared ZnS-HQ QDC. ^{1}H NMR (600 MHz, DMSO) δ 8.78 (s, 1H), 8.29 – 8.25 (m, 1H), 7.61 (s, 1H), 7.43 – 7.38 (m, 1H), 7.04 (d, J = 15.2 Hz, 1H), 6.76 (d, J = 13.5 Hz, 1H).

References:

1. Roy, S.; Bhandari, S.; Chattopadhyay, A. Quantum Dot Surface Mediated Unprecedented Reaction of Zn^{2+} and Copper Quinolate Complex. *J. Phys. Chem. C* **2015**, *119*, 21191–21197.
2. Bhandari, S.; Roy, S.; Chattopadhyay, A. Enhanced photoluminescence and thermal stability of zinc quinolate following complexation on the surface of quantum dots. *RSC Adv*. **2014**, *4*, 24217-24221.