

Electronic Supplementary Information

Fluorescence Quenching of the N-Methylquinolinium Cation by Pairs of Water or Alcohol Molecules

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Contents

	Page
Title page and contents	S1
Kinetic model	S2
Figure 1S. Absorption and fluorescence spectra of MQ^+ in water.....	S5
Figure 2S. Absorption and fluorescence spectra of MQ^+ in methanol.....	S5
Figure 3S. Absorption and fluorescence spectra of MQ^+ in ethanol.....	S6
Figure 4S. Fluorescence spectra of MQ^+ in acetonitrile, water, methanol and ethanol.....	S6
Figure 5S. Influence of water on the fluorescence of MQ^+ in acetonitrile.....	S7
Figure 6S. Influence of ethanol on the fluorescence of MQ^+ in acetonitrile.....	S8
Figure 7S. Influence of 1-propanol on the fluorescence of MQ^+ in acetonitrile.....	S9
Figure 8S. Influence of 1,2-ethanediol on the fluorescence of MQ^+ in acetonitrile.....	S10
Figure 9S. Influence of 1,3-propanediol on the fluorescence of MQ^+ in acetonitrile.....	S11
Figure 10S. Fluorescence of MQ^+ in acetonitrile with addition of 2,2,2-trifluoroethanol.....	S12
Figure 11S. Fluorescence decay of MQ^+ in acetonitrile with addition of alcohols.....	S12
Figure 12S. PCGA results of the fluorescence of MQ^+ in acetonitrile with water.....	S13
Figure 13S. PCGA results of the fluorescence of MQ^+ in acetonitrile with ethanol.....	S14
Figure 14S. PCGA results of the fluorescence of MQ^+ in acetonitrile with 1-propanol.....	S15
Figure 15S. PCGA results of the fluorescence of MQ^+ in acetonitrile with 1,2-ethanediol.....	S16
Figure 16S. PCGA results of the fluorescence of MQ^+ in acetonitrile with 1,3-propanediol.....	S17
Figure 17S. Atom numbering for the complex $\text{MQ}^+-2\text{H}_2\text{O}$	S18
Table 1S. Atomic coordinates for the optimized geometry of $\text{MQ}^+-2\text{H}_2\text{O}$ in the ground state.....	S19
Table 2S. Atomic coordinates for the optimized geometry of $\text{MQ}^+-2\text{H}_2\text{O}$ in the excited state.....	S20

Kinetic model

From Scheme 1, the exciplex formation equilibrium constant K and the excited-state concentrations of MQ^{+*} and E^* are given by eqs S1 to S3, where $[\text{T}^*]$ is the total concentration of excited species (eq S4).

$$K = \frac{[\text{E}^*]}{[\text{MQ}^{+*}][\text{ROH}]} \quad (\text{S1})$$

$$[\text{MQ}^{+*}] = \frac{[\text{T}^*]}{1 + K [\text{ROH}]} \quad (\text{S2})$$

$$[\text{E}^*] = \frac{K [\text{ROH}][\text{T}^*]}{1 + K [\text{ROH}]} \quad (\text{S3})$$

$$[\text{T}^*] = [\text{MQ}^{+*}] + [\text{E}^*] \quad (\text{S4})$$

The time dependence of $[\text{T}^*]$ after a short light pulse is given by:

$$-\frac{d[\text{T}^*]}{dt} = k_{\text{MQ}} [\text{MQ}^{+*}] + (k_{\text{E}} + k_{\text{q}} [\text{ROH}]) [\text{E}^*] \quad (\text{S5})$$

Integration of eq S5, together with eqs S2 and S3, leads to relations S6 and S7, where $[\text{T}^*]_0$ is the initial concentration of excited species.

$$[\text{T}^*] = [\text{T}^*]_0 e^{-k t} \quad (\text{S6})$$

$$k = \tau^{-1} = \frac{k_{\text{MQ}} + K k_{\text{E}} [\text{ROH}] + K k_{\text{q}} [\text{ROH}]^2}{1 + K [\text{ROH}]} \quad (\text{S7})$$

In the absence of quenchers, $\tau^0 = 1/k_{\text{MQ}}$, and therefore:

$$\frac{\tau^0}{\tau} = \frac{1 + \frac{K k_{\text{E}}}{k_{\text{MQ}}} [\text{ROH}] + \frac{K k_{\text{q}}}{k_{\text{MQ}}} [\text{ROH}]^2}{1 + K [\text{ROH}]} \quad (\text{S8})$$

From eqs S6, S2, and S3, the time dependence of $[\mathbf{MQ}^{+*}]$ and $[\mathbf{E}^*]$ can be easily calculated. Both show, like $[\mathbf{T}^*]$, a monoexponential decay with rate constant k , which displays a complex dependence on the hydroxy compound concentration (eq S7).

The fluorescence spectra of \mathbf{MQ}^{+*} and \mathbf{E}^* (vectors $\mathbf{F}_{\mathbf{MQ}}$ and $\mathbf{F}_{\mathbf{E}}$) depend on the steady-state (ss) concentrations of these species and are given by relations S9 and S10:

$$\mathbf{F}_{\mathbf{MQ}} = \chi^{\mathbf{MQ}} k_r^{\mathbf{MQ}} [\mathbf{MQ}^{+*}]_{\text{ss}} \quad (\text{S9})$$

$$\mathbf{F}_{\mathbf{E}} = \chi^{\mathbf{E}} k_r^{\mathbf{E}} [\mathbf{E}^*]_{\text{ss}} \quad (\text{S10})$$

In these equations, $k_r^{\mathbf{MQ}}$ and $k_r^{\mathbf{E}}$ are the radiative deactivation constants of \mathbf{MQ}^{+*} and \mathbf{E}^* , and the vectors $\chi^{\mathbf{MQ}}$ and $\chi^{\mathbf{E}}$ are the fluorescence emission spectra of \mathbf{MQ}^{+*} and \mathbf{E}^* with the area normalized to unity, multiplied by a common instrumental factor. $[\mathbf{MQ}^{+*}]_{\text{ss}}$ and $[\mathbf{E}^*]_{\text{ss}}$ are the steady-state concentrations of the respective species, obtained under continuous illumination.

Integration of eq S6 between time 0 and ∞ gives the steady-state concentration of the excited species, $[\mathbf{T}^*]_{\text{ss}}$. Substitution of $[\mathbf{T}^*]_{\text{ss}}$ into eqs S2 and S3 gives the steady-state concentrations $[\mathbf{MQ}^{+*}]_{\text{ss}}$ and $[\mathbf{E}^*]_{\text{ss}}$, which substituted into eqs S9 and S10, yield:

$$\mathbf{F}_{\mathbf{MQ}} = \chi^{\mathbf{MQ}} \frac{k_r^{\mathbf{MQ}}}{k_{\mathbf{MQ}}} [\mathbf{T}^*]_0 \frac{1}{1 + \frac{K k_{\mathbf{E}}}{k_{\mathbf{MQ}}} [\text{ROH}] + \frac{K k_{\mathbf{q}}}{k_{\mathbf{MQ}}} [\text{ROH}]^2} \quad (\text{S11})$$

$$\mathbf{F}_{\mathbf{E}} = \chi^{\mathbf{E}} \frac{k_r^{\mathbf{E}}}{k_{\mathbf{E}}} [\mathbf{T}^*]_0 \frac{\frac{K k_{\mathbf{E}}}{k_{\mathbf{MQ}}} [\text{ROH}]}{1 + \frac{K k_{\mathbf{E}}}{k_{\mathbf{MQ}}} [\text{ROH}] + \frac{K k_{\mathbf{q}}}{k_{\mathbf{MQ}}} [\text{ROH}]^2} \quad (\text{S12})$$

The first factors of eqs S11 and S12 define $\mathbf{F}_{\mathbf{MQ}}^0$ and $\mathbf{F}_{\mathbf{E}}^0$, the fluorescence spectra that would be obtained for \mathbf{MQ}^{+*} and \mathbf{E}^* if each absorbed photon formed an excited molecule of the respective species and only the unimolecular deactivation of these species would be operative:

$$\mathbf{F}_{\mathbf{MQ}}^0 = \chi^{\mathbf{MQ}} \frac{k_r^{\mathbf{MQ}}}{k_{\mathbf{MQ}}} [\mathbf{T}^*]_0 \quad (\text{S13})$$

$$\mathbf{F}_E^0 = \chi^E \frac{k_r^E}{k_E} [\mathbf{T}^*]_0 \quad (\text{S14})$$

The observed fluorescence spectrum is therefore:

$$\mathbf{F} = \mathbf{F}_{\text{MQ}} + \mathbf{F}_E = C_{\text{MQ}} \mathbf{F}_{\text{MQ}}^0 + C_E \mathbf{F}_E^0 \quad (\text{S15})$$

where the coefficients C_{MQ} and C_E , which represent the contributions of MQ^{+*} and E^* spectra to the experimental spectrum, are given by:

$$C_{\text{MQ}} = \frac{1}{1 + \frac{K k_E}{k_{\text{MQ}}} [\text{ROH}] + \frac{K k_q}{k_{\text{MQ}}} [\text{ROH}]^2} \quad (\text{S16})$$

$$C_E = \frac{\frac{K k_E}{k_{\text{MQ}}} [\text{ROH}]}{1 + \frac{K k_E}{k_{\text{MQ}}} [\text{ROH}] + \frac{K k_q}{k_{\text{MQ}}} [\text{ROH}]^2} \quad (\text{S17})$$

We denote by Φ_{MQ}^0 the fluorescence quantum yield of MQ^+ in ACN in the absence of quenchers ($\Phi_{\text{MQ}}^0 = k_r^{\text{MQ}}/k_{\text{MQ}}$) and by η_E^0 the fluorescence quantum efficiency of E^* if only the unimolecular photophysical deactivation of this excited species would be operative ($\eta_E^0 = k_r^E/k_E$). As \mathbf{F}_{MQ}^0 and \mathbf{F}_E^0 are normalized to the same concentration of excited species (eqs S13 and S14), the ratio of their integrated areas equals the ratio of fluorescence quantum yields:

$$\frac{\int \mathbf{F}_{\text{MQ}}^0 d\tilde{\nu}}{\int \mathbf{F}_E^0 d\tilde{\nu}} = \frac{\Phi_{\text{MQ}}^0}{\eta_E^0} \quad (\text{S18})$$

From the experimental value of this ratio and the known value of Φ_{MQ}^0 , we calculate η_E^0 , which together with k_E allows the determination of the radiative and nonradiative deactivation constant of the exciplex:

$$k_r^E = \eta_E^0 k_E \quad (\text{S19})$$

$$k_{nr}^E = k_E - k_r^E \quad (\text{S20})$$

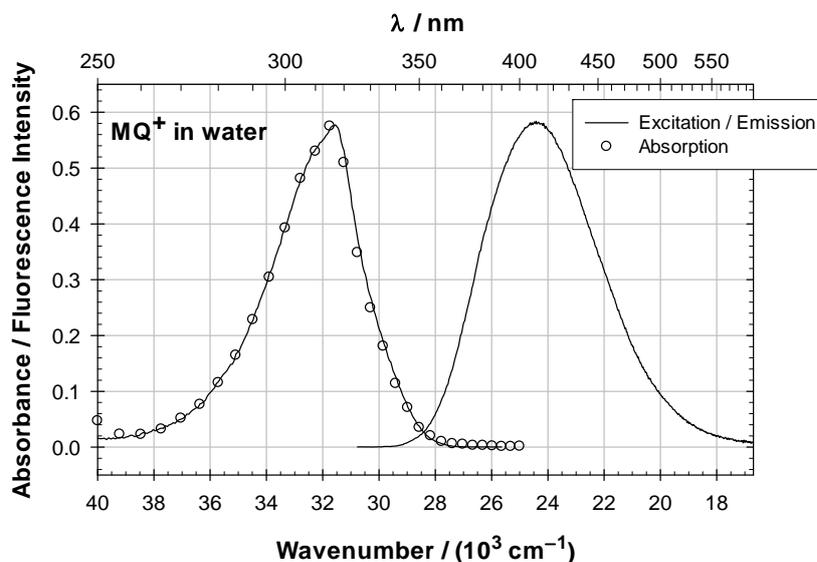


Figure 1S. Normalized absorption, fluorescence excitation, and fluorescence emission spectra of the N-methylquinolinium cation in water. $[\text{MQ}^+] = 9.29 \times 10^{-6} \text{ M}$ (fluorescence spectra) and $[\text{MQ}^+] = 7.65 \times 10^{-5} \text{ M}$ (absorption spectrum). $\bar{\nu}_{\text{excitation}} = 31950 \text{ cm}^{-1}$. $\bar{\nu}_{\text{emission}} = 24630 \text{ cm}^{-1}$.

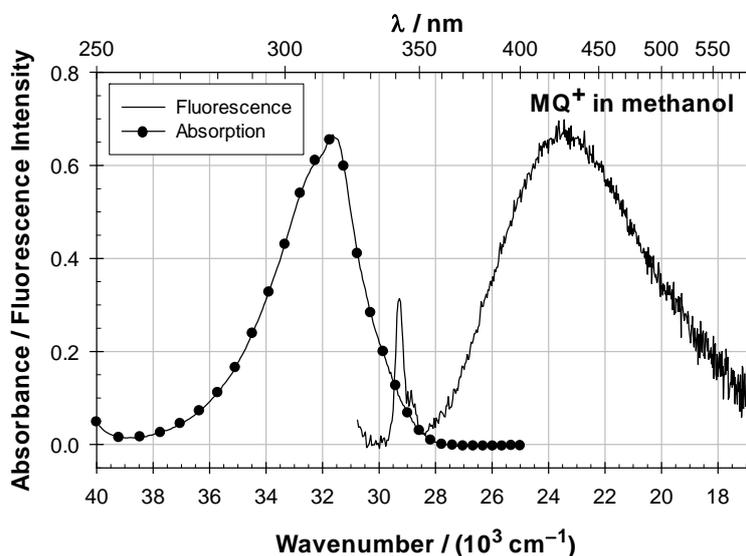


Figure 2S. Normalized absorption and fluorescence emission spectra of the N-methylquinolinium cation in methanol, and solvent Raman band. $[\text{MQ}^+] = 9.03 \times 10^{-6} \text{ M}$ (fluorescence spectrum) and $[\text{MQ}^+] = 8.45 \times 10^{-5} \text{ M}$ (absorption spectrum). $\bar{\nu}_{\text{excitation}} = 31950 \text{ cm}^{-1}$.

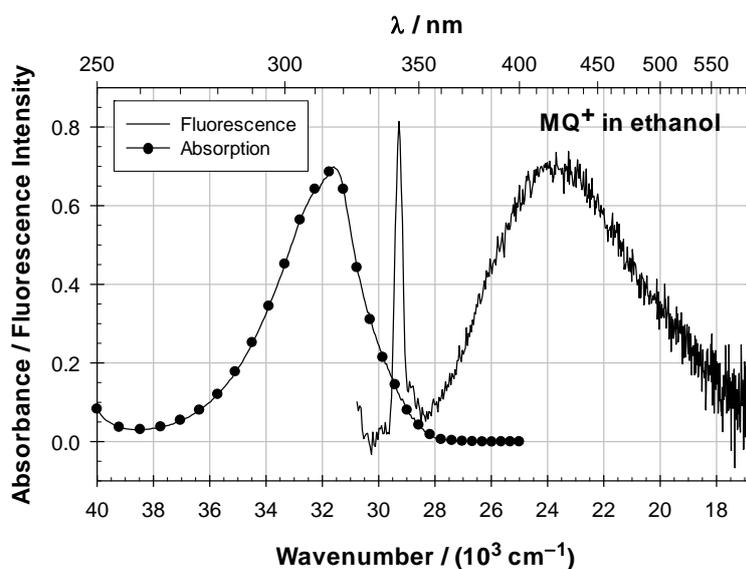


Figure 3S. Normalized absorption and fluorescence emission spectra of the N-methylquinolinium cation in ethanol, and solvent Raman band. $[MQ^+] = 9.86 \times 10^{-6}$ M (fluorescence spectrum) and $[MQ^+] = 9.23 \times 10^{-5}$ M (absorption spectrum). $\tilde{\nu}_{\text{excitation}} = 31950 \text{ cm}^{-1}$.

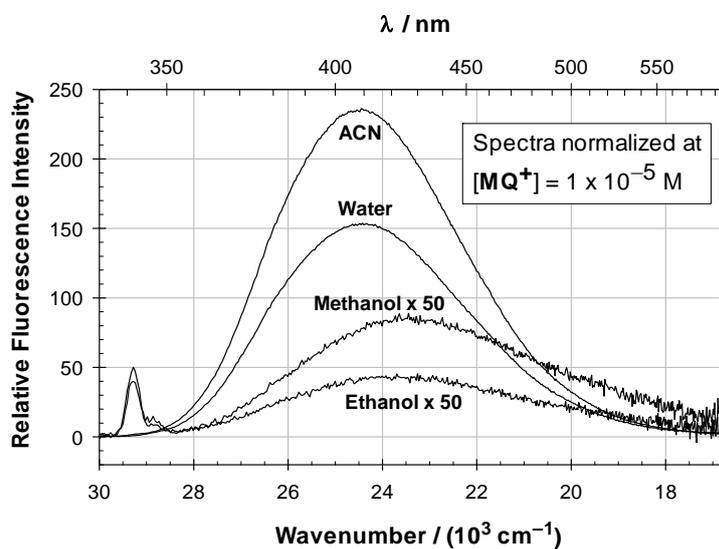


Figure 4S. Fluorescence emission spectra of the N-methylquinolinium cation in acetonitrile, water, methanol and ethanol, normalized at MQ^+ concentration of 1×10^{-5} M, and alcohol Raman band. The intensity of the spectra in methanol and ethanol were multiplied by a factor of 50. $\tilde{\nu}_{\text{excitation}} = 31950 \text{ cm}^{-1}$.

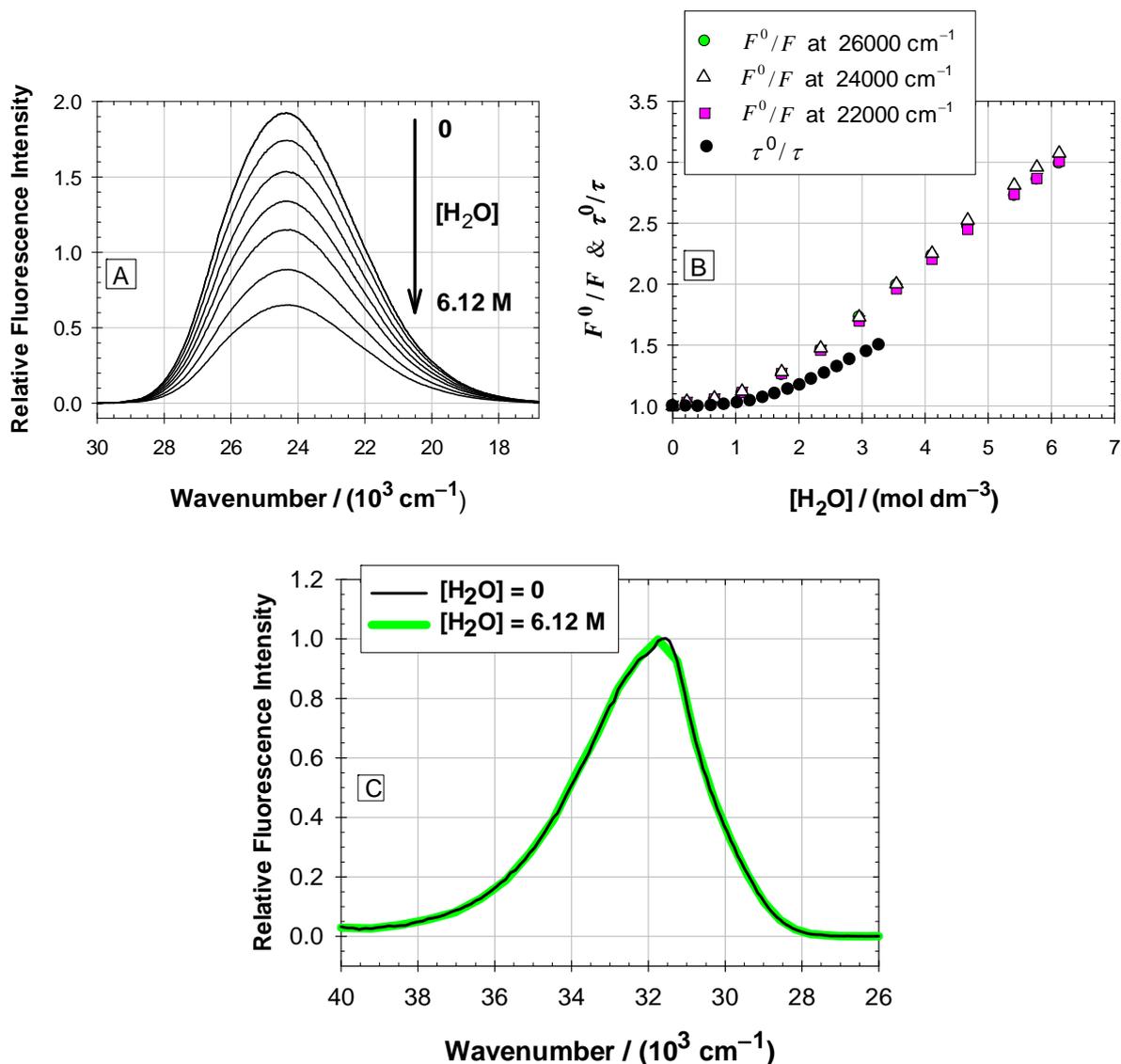


Figure 5S. Influence of water on the fluorescence spectra of MQ^+ in acetonitrile: (A) Fluorescence emission spectra with increasing concentration of water in the range 0 to 6.12 mol/dm^3 ($\tilde{\nu}_{\text{exc}} = 31950 \text{ cm}^{-1}$); (B) Influence of water concentration on the fluorescence intensity ratio F^0/F at various emission wavenumbers ($\tilde{\nu}_{\text{exc}} = 31950 \text{ cm}^{-1}$), and on the fluorescence lifetime ratio τ^0/τ ($\tilde{\nu}_{\text{exc}} = 32450 \text{ cm}^{-1}$, $\tilde{\nu}_{\text{em}} = 24400 \text{ cm}^{-1}$); (C) Normalized fluorescence excitation spectra in pure acetonitrile and with addition of 6.12 mol/dm^3 of water ($\tilde{\nu}_{\text{em}} = 24630 \text{ cm}^{-1}$). $[\text{MQ}^+] = 9.13 \times 10^{-6} \text{ mol/dm}^3$ for the steady-state measurements and $1.04 \times 10^{-4} \text{ mol/dm}^3$ for the lifetime measurements.

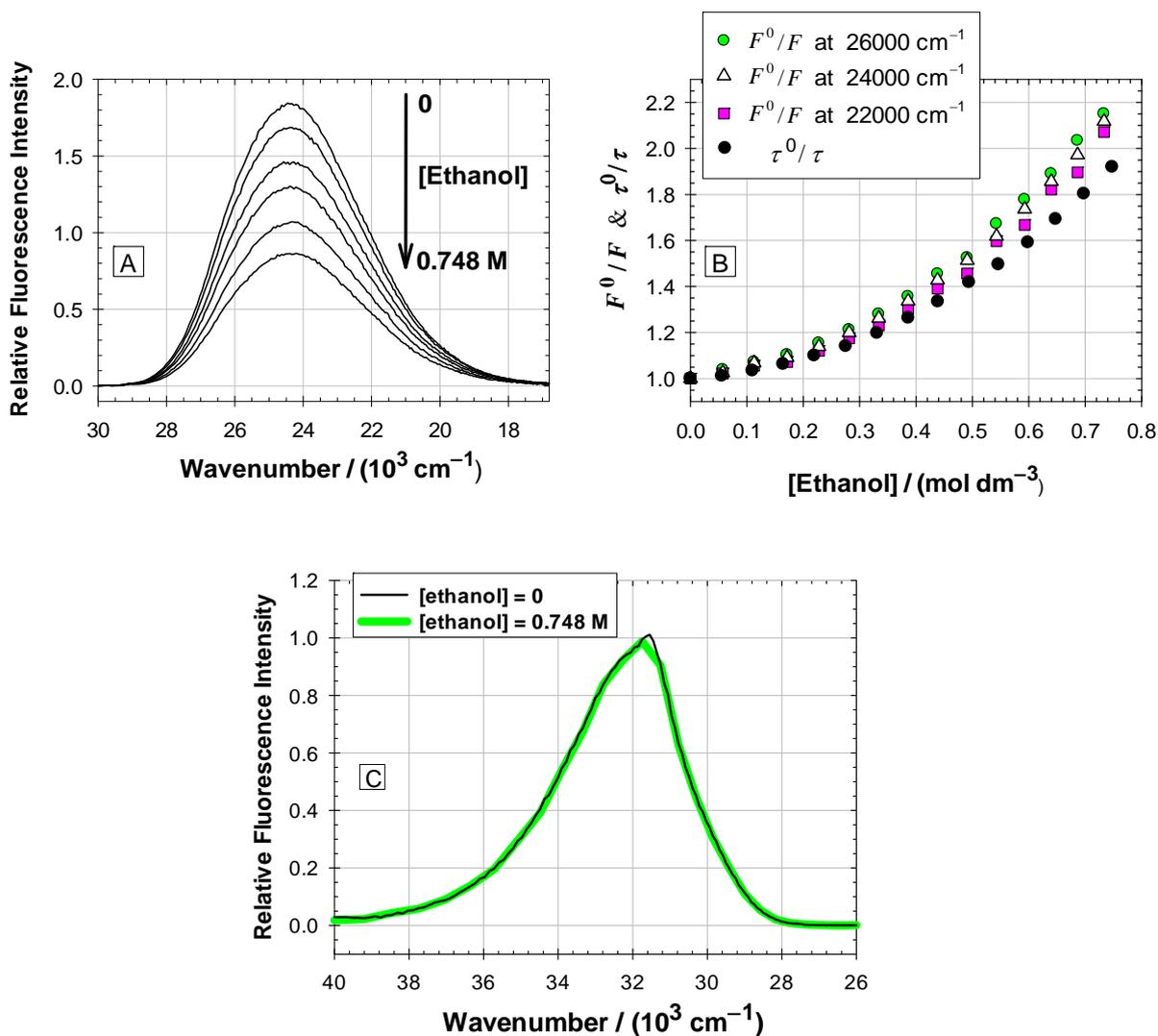


Figure 6S. Influence of ethanol on the fluorescence spectra of MQ⁺ in acetonitrile: (A) Fluorescence emission spectra with increasing concentration of ethanol in the range 0 to 0.748 mol/dm³ ($\tilde{\nu}_{\text{exc}} = 31950 \text{ cm}^{-1}$); (B) Influence of ethanol concentration on the fluorescence intensity ratio F^0/F at various emission wavenumbers ($\tilde{\nu}_{\text{exc}} = 31950 \text{ cm}^{-1}$), and on the fluorescence lifetime ratio τ^0/τ ($\tilde{\nu}_{\text{exc}} = 32450 \text{ cm}^{-1}$, $\tilde{\nu}_{\text{em}} = 24400 \text{ cm}^{-1}$); (C) Normalized fluorescence excitation spectra in pure acetonitrile and with addition of 0.748 mol/dm³ of ethanol ($\tilde{\nu}_{\text{em}} = 24630 \text{ cm}^{-1}$). $[\text{MQ}^+] = 8.25 \times 10^{-6} \text{ mol/dm}^3$ for the steady-state measurements and $1.02 \times 10^{-4} \text{ mol/dm}^3$ for the lifetime measurements.

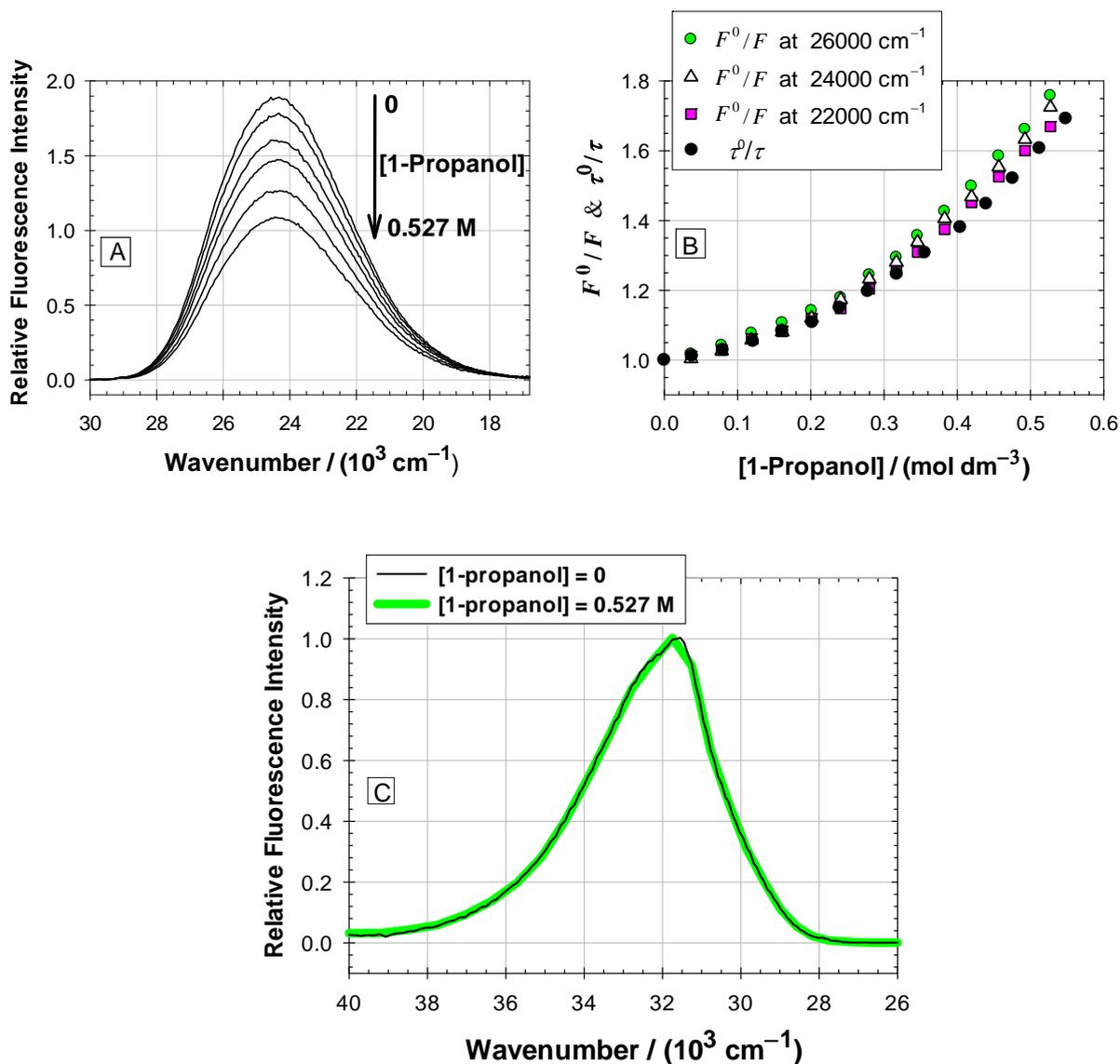


Figure 7S. Influence of 1-propanol on the fluorescence spectra of MQ^+ in acetonitrile: (A) Fluorescence emission spectra with increasing concentration of 1-propanol in the range 0 to 0.527 mol/dm^3 ($\tilde{\nu}_{\text{exc}} = 31950 \text{ cm}^{-1}$); (B) Influence of 1-propanol concentration on the fluorescence intensity ratio F^0/F at various emission wavenumbers ($\tilde{\nu}_{\text{exc}} = 31950 \text{ cm}^{-1}$), and on the fluorescence lifetime ratio τ^0/τ ($\tilde{\nu}_{\text{exc}} = 32450 \text{ cm}^{-1}$, $\tilde{\nu}_{\text{em}} = 24400 \text{ cm}^{-1}$); (C) Normalized fluorescence excitation spectra in pure acetonitrile and with addition of 0.527 mol/dm^3 of 1-propanol ($\tilde{\nu}_{\text{em}} = 24630 \text{ cm}^{-1}$). $[\text{MQ}^+] = 8.95 \times 10^{-6} \text{ mol/dm}^3$ for the steady-state measurements and $1.00 \times 10^{-4} \text{ mol/dm}^3$ for the lifetime measurements.

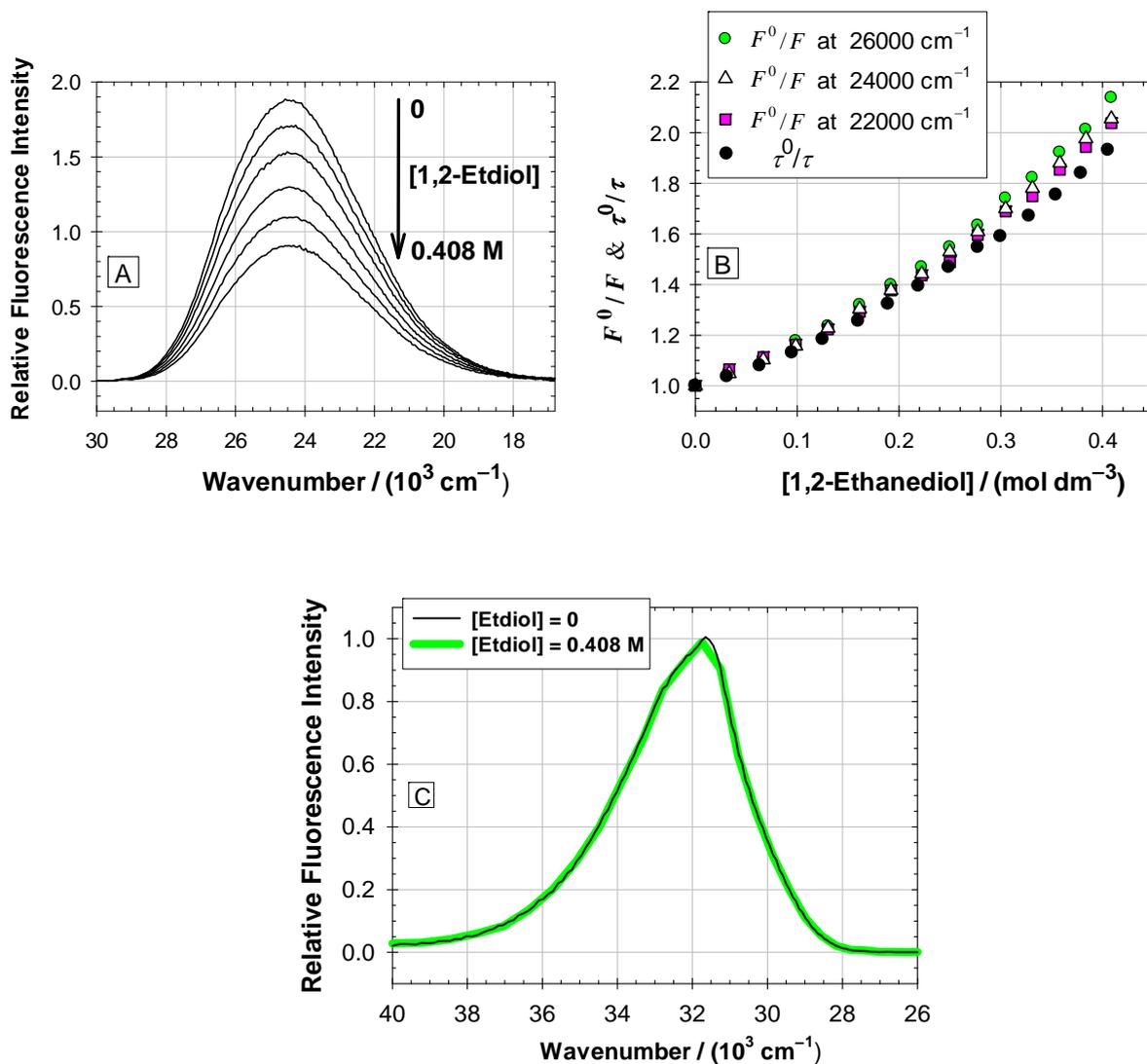


Figure 8S. Influence of 1,2-ethanediol on the fluorescence spectra of MQ^+ in acetonitrile: (A) Fluorescence emission spectra with increasing concentration of 1,2-ethanediol in the range 0 to 0.408 mol/dm^3 ($\tilde{\nu}_{\text{exc}} = 31950 \text{ cm}^{-1}$); (B) Influence of 1,2-ethanediol concentration on the fluorescence intensity ratio F^0/F at various emission wavenumbers ($\tilde{\nu}_{\text{exc}} = 31950 \text{ cm}^{-1}$), and on the fluorescence lifetime ratio τ^0/τ ($\tilde{\nu}_{\text{exc}} = 32450 \text{ cm}^{-1}$, $\tilde{\nu}_{\text{em}} = 24400 \text{ cm}^{-1}$); (C) Normalized fluorescence excitation spectra in pure acetonitrile and with addition of 0.408 mol/dm^3 of 1,2-ethanediol ($\tilde{\nu}_{\text{em}} = 24630 \text{ cm}^{-1}$). $[\text{MQ}^+] = 8.27 \times 10^{-6} \text{ mol/dm}^3$ for the steady-state measurements and $9.95 \times 10^{-5} \text{ mol/dm}^3$ for the lifetime measurements.

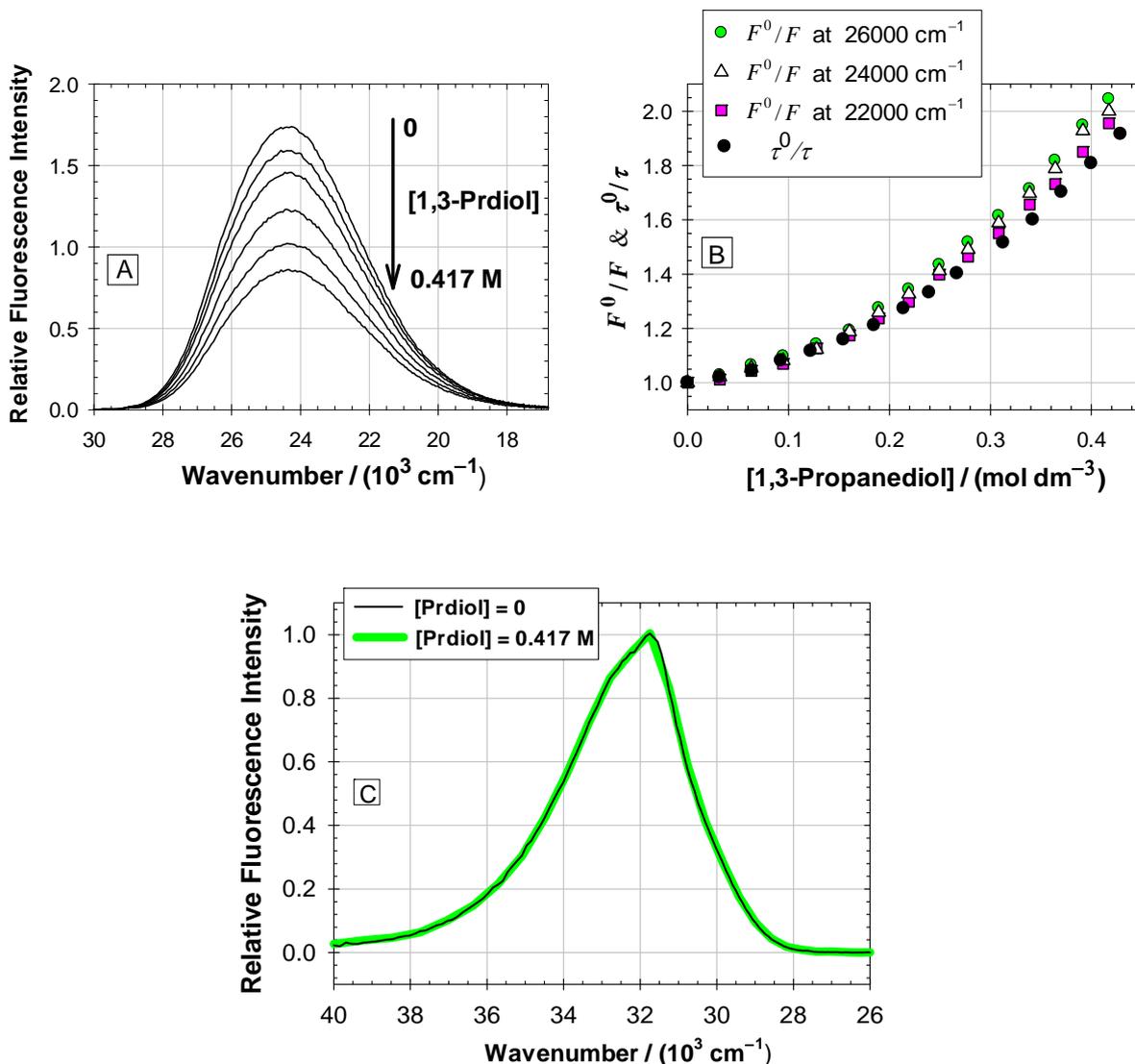


Figure 9S. Influence of 1,3-propanediol on the fluorescence spectra of MQ^+ in acetonitrile: (A) Fluorescence emission spectra with increasing concentration of 1,3-propanediol in the range 0 to 0.417 mol/dm^3 ($\tilde{\nu}_{\text{exc}} = 31950 \text{ cm}^{-1}$); (B) Influence of 1,3-propanediol concentration on the fluorescence intensity ratio F^0/F at various emission wavenumbers ($\tilde{\nu}_{\text{exc}} = 31950 \text{ cm}^{-1}$), and on the fluorescence lifetime ratio τ^0/τ ($\tilde{\nu}_{\text{exc}} = 32450 \text{ cm}^{-1}$, $\tilde{\nu}_{\text{em}} = 24400 \text{ cm}^{-1}$); (C) Normalized fluorescence excitation spectra in pure acetonitrile and with addition of 0.417 mol/dm^3 of 1,3-propanediol ($\tilde{\nu}_{\text{em}} = 24630 \text{ cm}^{-1}$). $[\text{MQ}^+] = 7.52 \times 10^{-6} \text{ mol/dm}^3$ for the steady-state measurements and $9.96 \times 10^{-5} \text{ mol/dm}^3$ for the lifetime measurements.

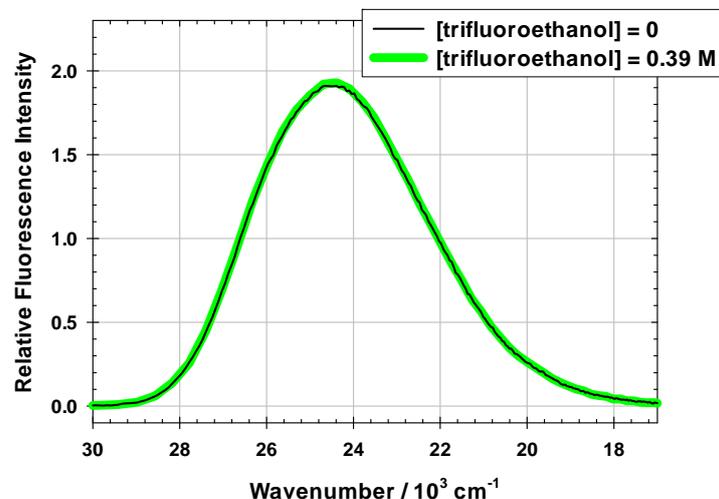


Figure 10S. Fluorescence emission spectra of the N-methylquinolinium cation in neat acetonitrile and with addition of 0.39 M of 2,2,2-trifluoroethanol. The spectra were not normalized. $[\text{MQ}^+] = 9.01 \times 10^{-6} \text{ M}$. $\bar{\nu}_{\text{excitation}} = 31950 \text{ cm}^{-1}$.

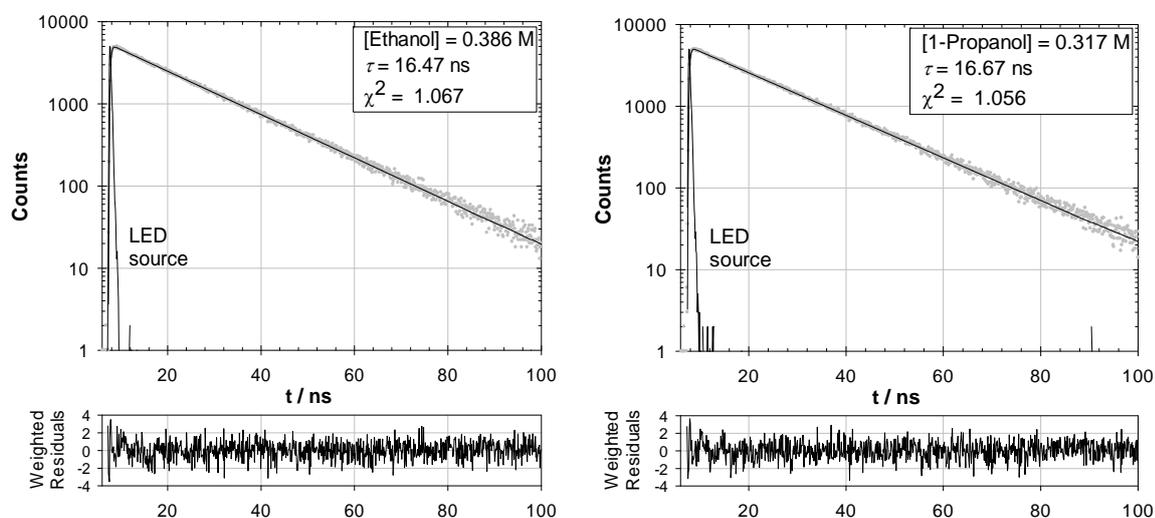


Figure 11S. Fluorescence decay of the N-methylquinolinium cation in acetonitrile with addition of 0.386 M ethanol (left, $[\text{MQ}^+] = 1.02 \times 10^{-4} \text{ M}$) and 0.317 M 1-propanol (right, $[\text{MQ}^+] = 1.00 \times 10^{-4} \text{ M}$), and LED source profile. The monoexponential fit and the weighted residuals are also shown. $\bar{\nu}_{\text{excitation}} = 32450 \text{ cm}^{-1}$. $\bar{\nu}_{\text{emission}} = 24400 \text{ cm}^{-1}$.

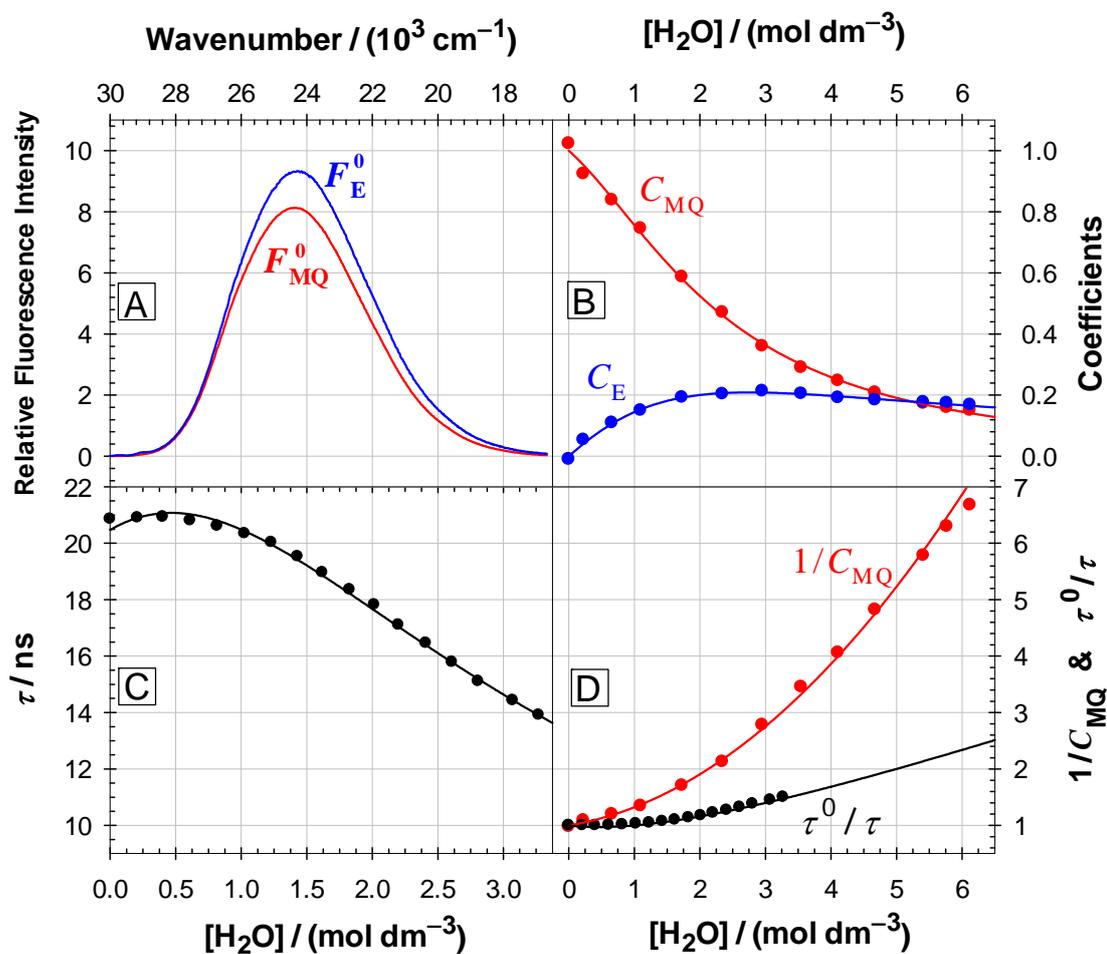


Figure 12S. Results of the principal component global analysis of the fluorescence spectra and lifetimes of MQ^+ in acetonitrile in the presence of water: (A) Component spectra obtained, associated to MQ^{+*} (F_{MQ}^0) and the exciplex (F_{E}^0); (B) the coefficients C_{MQ} and C_{E} representing the contributions of MQ^{+*} and E^* spectra to the experimental spectrum, and the fit lines; (C) the experimental fluorescence lifetimes and the fit line; (D) the experimental values of $1/C_{\text{MQ}}$ and τ^0/τ , and the calculated fits.

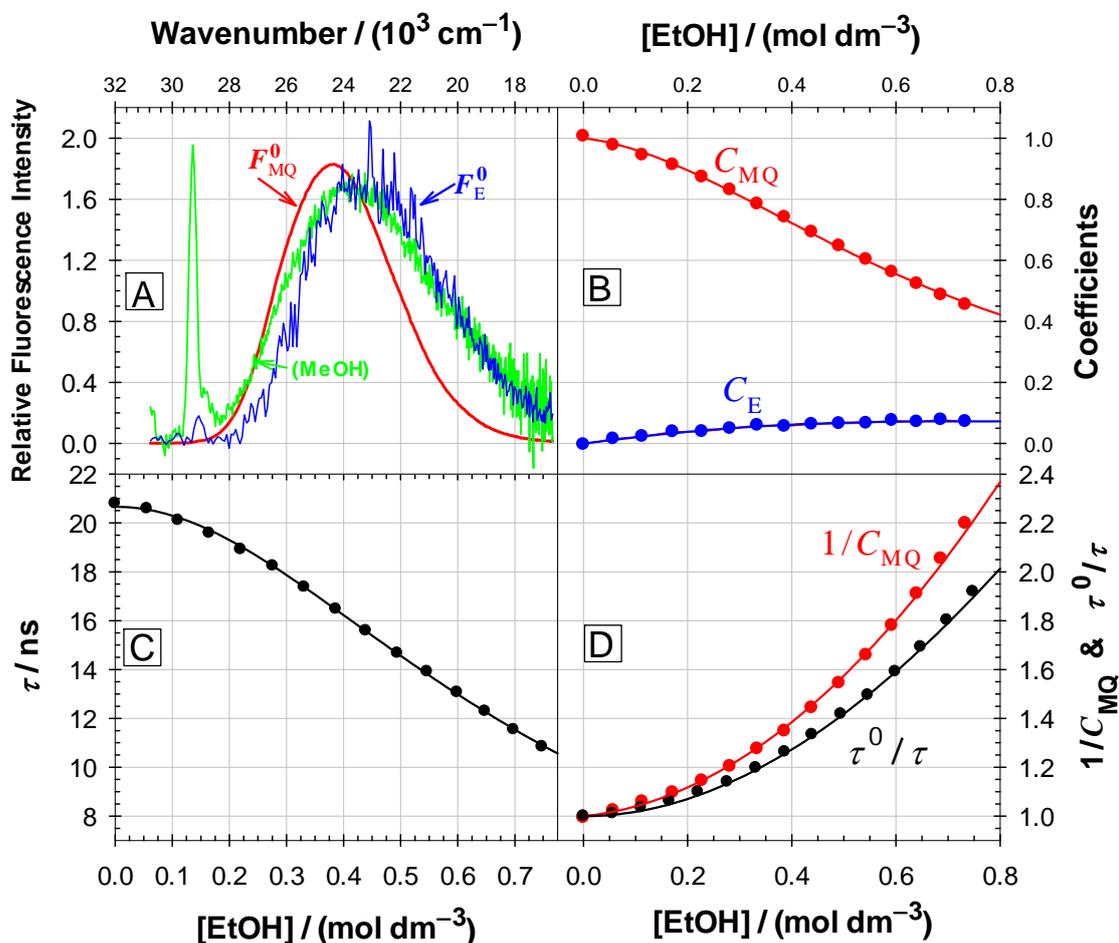


Figure 13S. Results of the principal-component global analysis of the fluorescence spectra and lifetimes of MQ^+ in acetonitrile in the presence of ethanol: (A) Normalized component spectra obtained, associated to MQ^{+*} (F_{MQ}^0 , red line) and the exciplex (F_{E}^0 , blue line), together with the fluorescence spectrum of MQ^+ in neat ethanol ($\nu_{\text{excitation}} = 31950 \text{ cm}^{-1}$, green line, with solvent Raman band); (B) the coefficients C_{MQ} and C_{E} representing the contributions of MQ^{+*} and E^* spectra to the experimental spectrum, and the fit lines; (C) the experimental fluorescence lifetimes and the fit line; (D) the experimental values of $1/C_{\text{MQ}}$ and τ^0/τ , and the calculated fits.

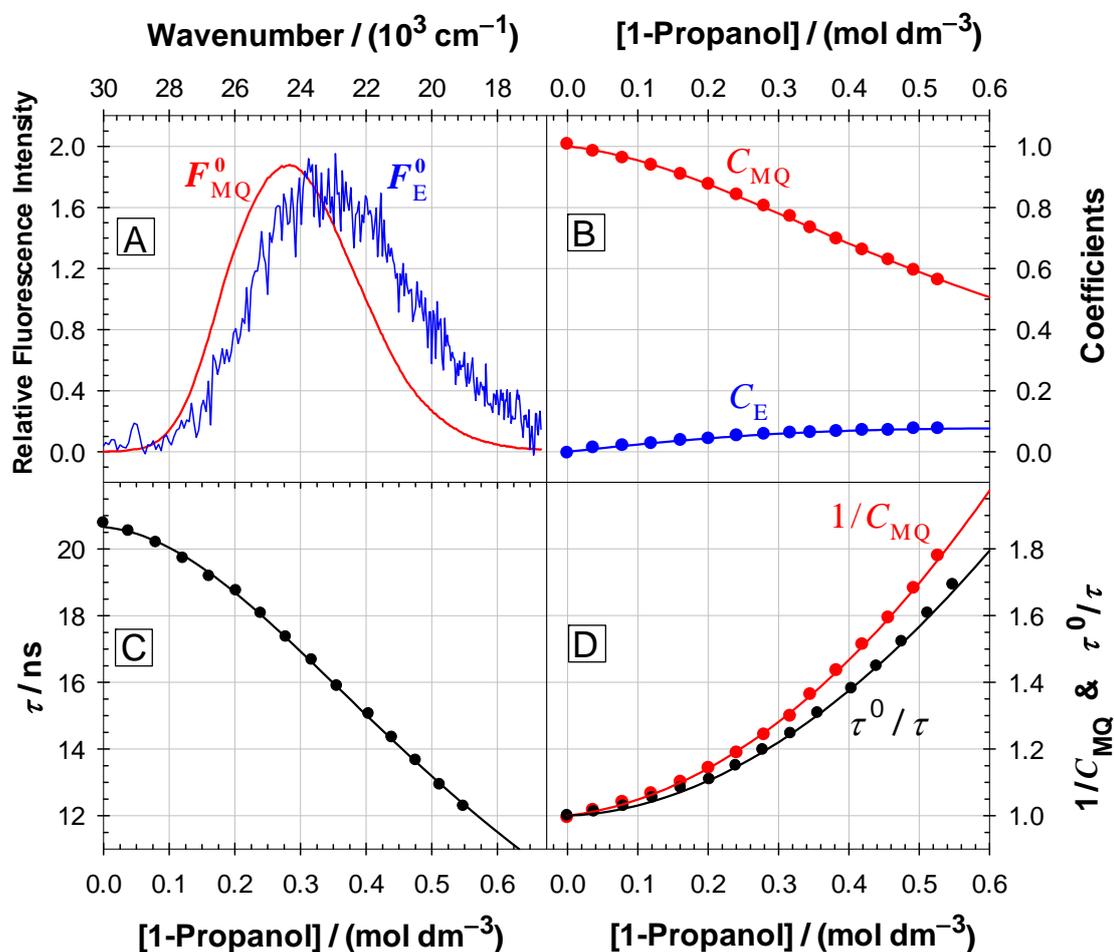


Figure 14S. Results of the principal component global analysis of the fluorescence spectra and lifetimes of MQ^+ in acetonitrile in the presence of 1-propanol: (A) Normalized component spectra obtained, associated to MQ^{+*} (F_{MQ}^0) and the exciplex (F_{E}^0); (B) the coefficients C_{MQ} and C_{E} representing the contributions of MQ^{+*} and E^* spectra to the experimental spectrum, and the fit lines; (C) the experimental fluorescence lifetimes and the fit line; (D) the experimental values of $1/C_{\text{MQ}}$ and τ^0/τ , and the calculated fits.

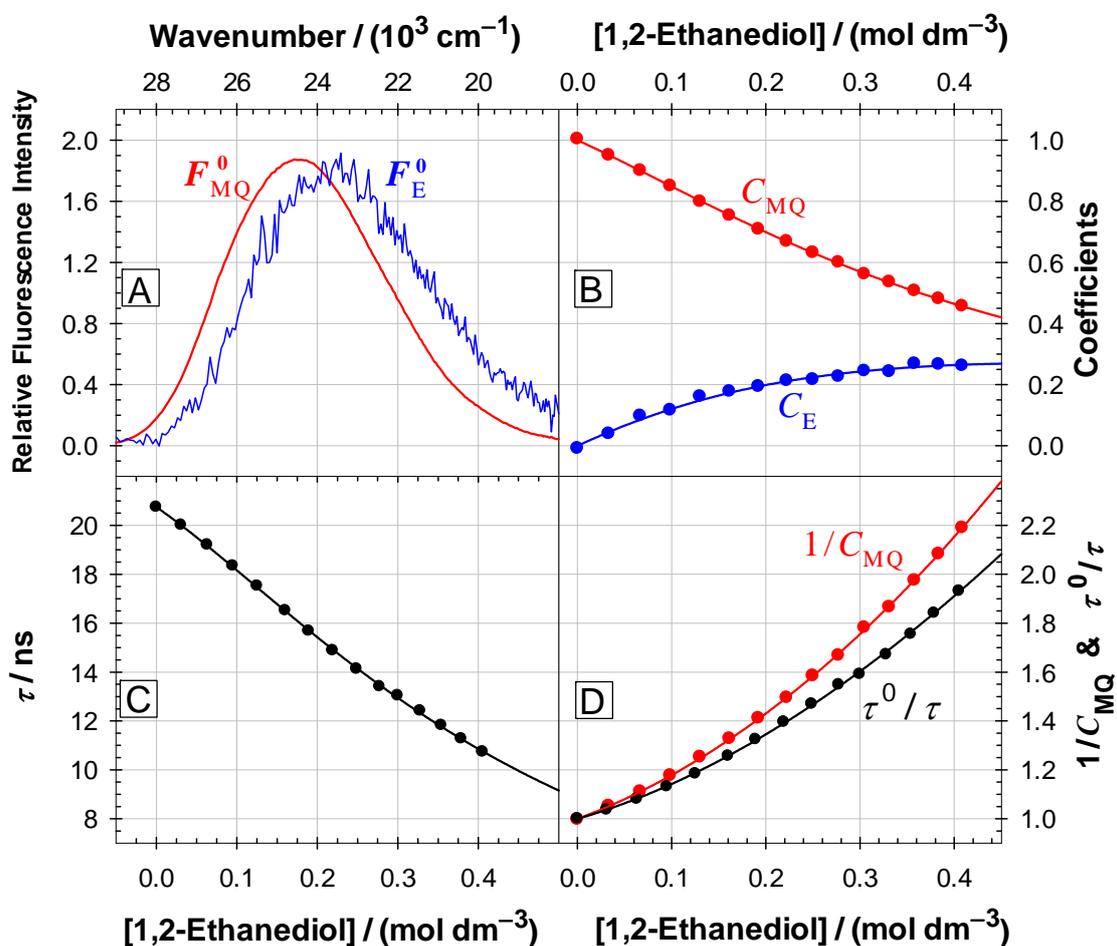


Figure 15S. Results of the principal component global analysis of the fluorescence spectra and lifetimes of MQ^+ in acetonitrile in the presence of 1,2-ethanediol: (A) Normalized component spectra obtained, associated to MQ^{+*} (F_{MQ}^0) and the exciplex (F_{E}^0); (B) the coefficients C_{MQ} and C_{E} representing the contributions of MQ^{+*} and E^* spectra to the experimental spectrum, and the fit lines; (C) the experimental fluorescence lifetimes and the fit line; (D) the experimental values of $1/C_{\text{MQ}}$ and τ^0/τ , and the calculated fits.

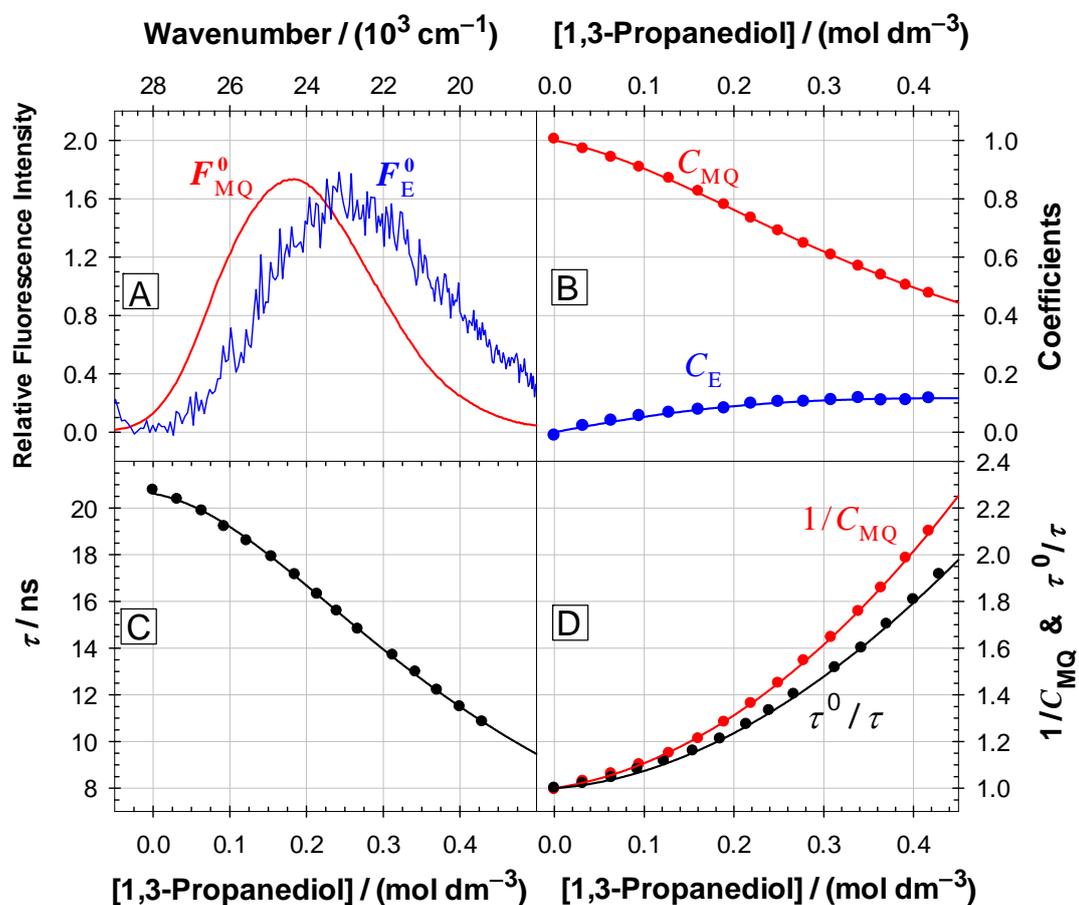


Figure 16S. Results of the principal component global analysis of the fluorescence spectra and lifetimes of MQ^+ in acetonitrile in the presence of 1,3-propanediol: (A) Normalized component spectra obtained, associated to MQ^{+*} (F_{MQ}^0) and the exciplex (F_{E}^0); (B) the coefficients C_{MQ} and C_{E} representing the contributions of MQ^{+*} and E^* spectra to the experimental spectrum, and the fit lines; (C) the experimental fluorescence lifetimes and the fit line; (D) the experimental values of $1/C_{\text{MQ}}$ and τ^0/τ , and the calculated fits.

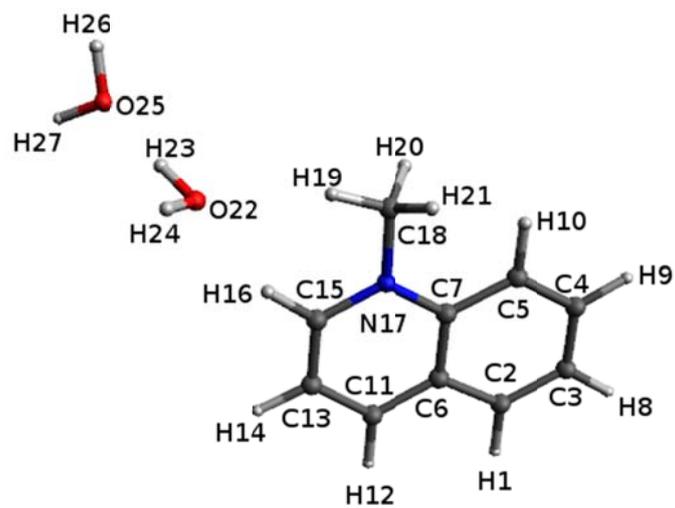


Figure 17S. Atom numbering for the complex of MQ⁺ with two water molecules.

Table 1S. Atomic Cartesian Coordinates for the B3LYP/aug-cc-pVTZ optimized geometry of the MQ⁺-2H₂O complex in the electronic ground state

Atom number	Atom type	x/Å	y/Å	z/Å
1	H	3.791569	1.838906	0.425678
2	C	3.287986	0.888509	0.314661
3	C	3.984654	-0.287867	0.389893
4	C	3.309775	-1.514386	0.243322
5	C	1.952987	-1.562768	0.023374
6	C	1.891709	0.883707	0.089751
7	C	1.222554	-0.364952	-0.057518
8	H	5.051285	-0.280833	0.561722
9	H	3.866862	-2.438721	0.304412
10	H	1.465598	-2.517880	-0.084444
11	C	1.141622	2.073129	0.006824
12	H	1.646767	3.023417	0.118420
13	C	-0.211958	2.022136	-0.212579
14	H	-0.813185	2.915511	-0.280884
15	C	-0.833226	0.784049	-0.352758
16	H	-1.898405	0.686282	-0.528851
17	N	-0.144821	-0.356849	-0.278685
18	C	-0.877476	-1.631021	-0.439345
19	H	-1.924364	-1.403090	-0.611724
20	H	-0.771595	-2.226704	0.464435
21	H	-0.472827	-2.177144	-1.288329
22	O	-3.832914	-0.062113	-0.888846
23	H	-4.531238	-0.103405	-0.207473
24	H	-4.297994	0.015103	-1.727324
25	O	-5.759254	-0.205215	1.139786
26	H	-6.303085	-0.982769	1.302427
27	H	-6.270053	0.544671	1.461468

Table 2S. Atomic Cartesian Coordinates for the B3LYP/aug-cc-pVTZ optimized geometry of the MQ⁺-2H₂O complex in the first-excited singlet state

Atom number	Atom type	x/Å	y/Å	z/Å
1	H	3.853973	1.741623	0.427688
2	C	3.309474	0.813673	0.309308
3	C	4.029395	-0.410101	0.375715
4	C	3.347019	-1.588527	0.226544
5	C	1.953925	-1.549455	0.011637
6	C	1.910035	0.884817	0.094733
7	C	1.223286	-0.319856	-0.058559
8	H	5.096243	-0.390856	0.542048
9	H	3.850257	-2.542686	0.270111
10	H	1.426416	-2.483893	-0.102301
11	C	1.212320	2.134055	0.034674
12	H	1.741124	3.065579	0.153033
13	C	-0.166043	2.086721	-0.179255
14	H	-0.746017	2.996454	-0.232050
15	C	-0.825578	0.893589	-0.328869
16	H	-1.888753	0.813271	-0.496714
17	N	-0.137792	-0.321286	-0.273011
18	C	-0.897141	-1.562777	-0.444700
19	H	-1.937401	-1.303770	-0.618704
20	H	-0.835946	-2.182213	0.451063
21	H	-0.529125	-2.126009	-1.302965
22	O	-3.883308	-0.100237	-0.890407
23	H	-4.587889	-0.151599	-0.218470
24	H	-4.340062	0.004262	-1.730251
25	O	-5.859159	-0.267966	1.117300
26	H	-6.436725	-1.027686	1.242550
27	H	-6.341966	0.489309	1.463525