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Low temperature fluorescence studies of crude petroleum oils.

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Supplemental Information:

Instrumentation details:

For lifetime analysis of the neat crude oil samples, a Time Correlated Single Photon Counting (TCSPC) system, (Time Harp 100, PicoQuant), coupled with a microscope (Olympus BX51) and a cooling stage was assembled in house (Figure S-1). The microscope had the illuminator lenses removed to maximize light throughput. The pulsed 405 nm laser (LDH-405, PicoQuant) was focused through a standard 10x objective (Olympus MPLAN 0.25NA) onto the sample held in a liquid nitrogen cooled, heating-freezing stage (Linkam TMS600). Fluorescence emission collected via the objective lens was filtered through a dichroic mirror unit which incorporated a 405 nm stop-line filter and a 410 nm long-pass filter to minimize scattered excitation light from entering the detection system. The emission passed through an outlet in the head of the microscope which was fitted with an adjustable iris and a filter holder for neutral density filters. The system was connected to the monochromator (model 9030, Sciencetech, Canada) by fibre optic cable (Ocean Optics QP1000-2-UV/VIS). Control of the signal intensity to the PMT detector (model H5783, Hamamatsu, Japan) was achieved using the iris and the input/output slits on the monochromator.

For the diluted oil, the system was modified to incorporate a fiber optic reflection probe (Ocean optics R400-7-UV/VIS) and a PicoHarp 300 TCSPC unit (Figure 1, main manuscript). The pulsed laser was coupled into the central fiber while the emission was collected by the six surrounding fibers. For measurement of steady-state emission spectra the fiber-optic probe was diverted to an Ocean Optics USB2000 spectrometer.

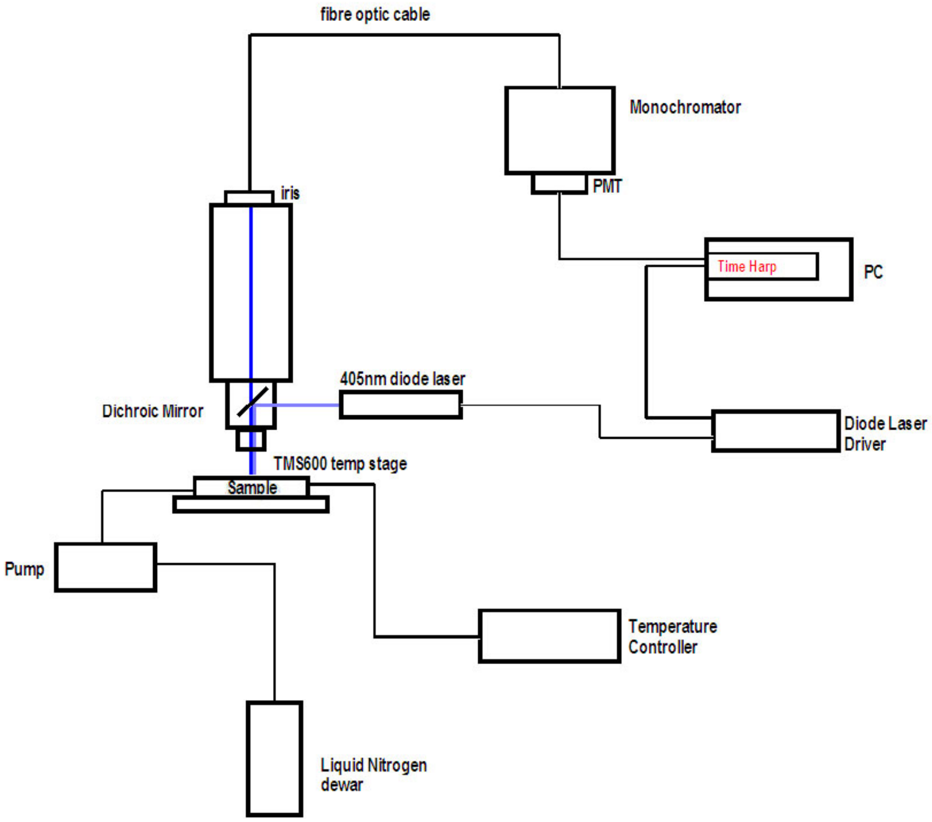

Figure S-1: Schematic of the second low temperature measurement system used for the analysis of the neat crude oils described in the manuscript text.

Measurement details:

The Instrument Response Function (IRF) was measured by collecting back scattered excitation light from the temperature cell quartz window with the 405 nm stopline and 410 nm long-pass filters removed from the emission path, and the monochromator first order wavelength set to 405 nm. For lifetime validation, a solution (10^{-5} M in 0.2 M phosphate buffer) of HPTS (8-hydroxy-1,3,6 tri-sulfonated pyrene) was employed. The lifetime of HPTS was validated using a second, cuvette based TCSPC system (Picoquant Fluotime 200) and this data was used to determine the accuracy of the temperature based lifetime system. All lifetime validation measurements were made at room temperature using non-degassed solutions.

Additional Spectral Data:

Most crude oils exhibit a broad spectral emission profile which increases in intensity (Figure S-2a) and is blue-shifted (Figure S-2b) with increasing dilution. At very high dilution ratios, the concentration of quenchers and fluorophores is decreased, thus reducing the rate of ET and quenching.

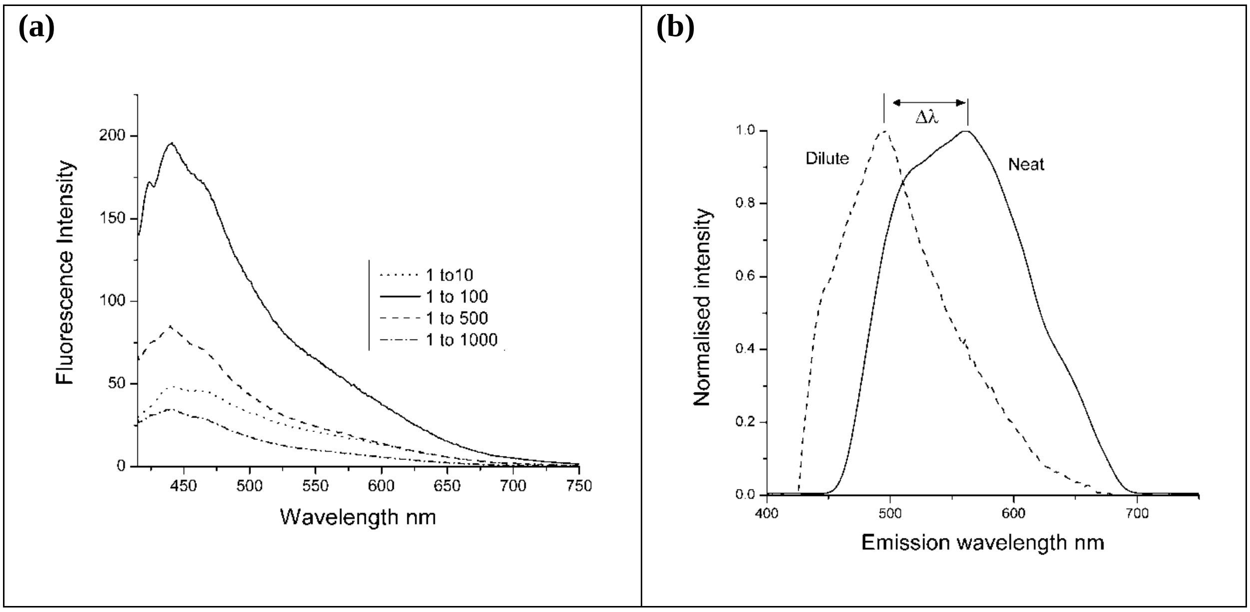

Figure S-2: (a) Emission spectra (uncorrected) as collected for the light oil 9197 at a range of dilutions. **(b)** Normalised emission spectra for heavy oil 7188 diluted with MeCH:MeCP.

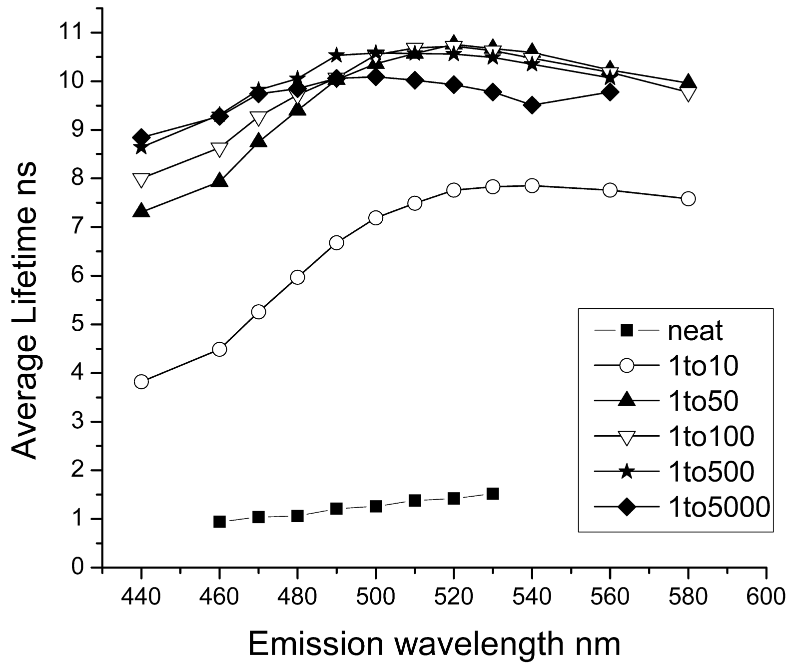

Figure S-3: Average lifetimes for the heavy oil 7188 diluted in MeCH:MeCP.

The variation in fluorescence lifetime (Figure S-3) for the heavy oils on dilution is quite dramatic, with the largest changes occurring between the neat and the 1:50 dilution, after which the changes in lifetime are much smaller.

Lowering the temperature results in red shifted emission spectra and the full width half maximum increases (Figure S-4). This we can attribute to a reduction in the rate of non-radiative decay via the internal conversion pathway described by the energy gap law. Thus we see more emission from the larger red emitting fluorophores at lower temperatures.

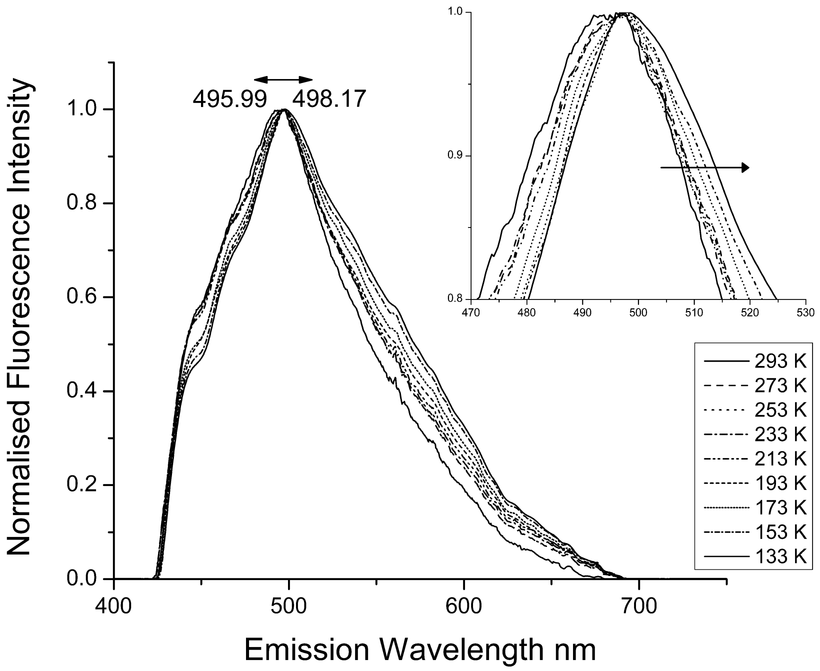

Figure S-4: Normalised emission spectra for diluted heavy oil 7033 (1:5000 in deoxygenated 3:2 meCH:MeCP) between 293 and 133 K.

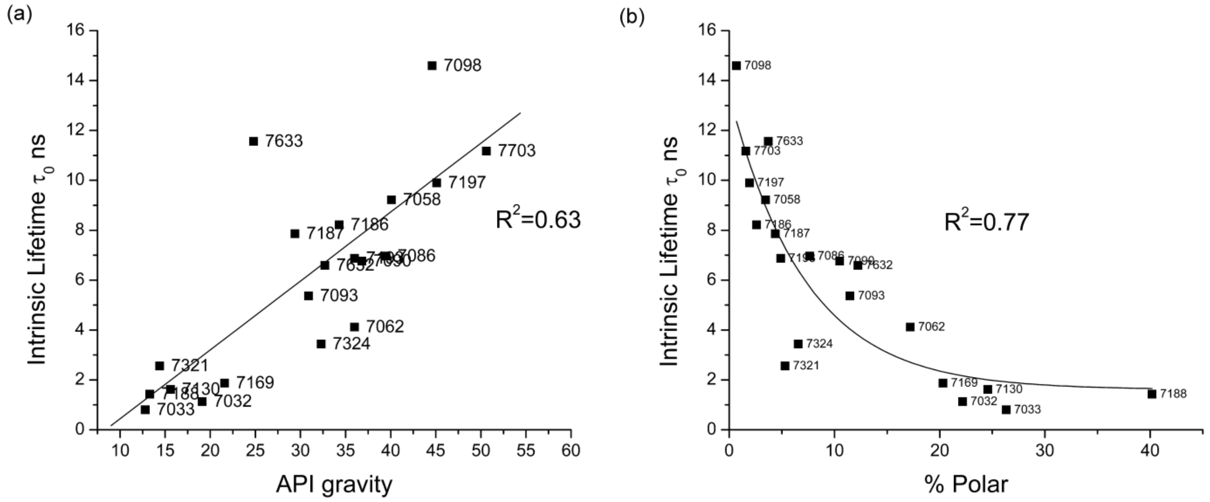

Figure S-5: (a) Correlation of intrinsic lifetimes to API gravity. A general positive trend with a high degree of scatter is observed, with two clear outliers. The changes in the photophysics can be attributed to asphaltene and wax; oil 7633 has a high wax content (13%) yet low polar and asphaltene content. Oil 7098 has a very low polar content (0.7%) despite its low density (high API). This may give enhanced viscosity-temperature effects. (b) Correlation to % Polar.

The τ_0 values determined at 500 nm generally increase with decreasing density (increasing API gravity) and a decrease with increasing polar content. However for both plots, a significant spread is found, reflecting the compositional complexity of the crude oil samples. The two major outliers in Figure S-5a, 7633 and 7098, have abnormally long lifetimes which originate from a combination of compositional effects: oil 7633 has a high wax content (13%), low polar, low aromatic (2.93%) and low asphaltene content (0.7%) despite a relatively high density, while oil 7098 has a very low polar (0.7%), aromatic (4.6%) and sulfur content (0.043%) despite having a low density (high API). So, like the room temperature measurements we cannot generate any accurate correlations between the intrinsic lifetime and the compositional data generated by the SARA analysis.[1-3]

Stern-Volmer Quenching Analysis:

To estimate the degree of both collisional and static quenching, the classic Stern-Volmer equation was modified to include a static quenching term:

$$\frac{\tau}{\tau_0} = (1 + K_{sv}[Q])(\exp(K_{st}[Q]))$$

Equation S-1

where K_{sv} is the pseudo Stern-Volmer constant, [Q] is the quencher concentration and K_{sv} is the pseudo static quenching constant. K_{sv} is equal to $k_q\tau_0$ where k_q is the pseudo collisional quenching constant and τ_0 is the longest lifetime reached on dilution by the de-oxygenated solvent. At the lowest temperatures (173-153 K), K_{sv} tends to zero and K_{st} increases dramatically. At this point, static processes are dominant and the modified Stern-Volmer relationship can now be written as:

$$\frac{\tau}{\tau_0} = \exp(K_{st}[Q])$$

Equation S-2

Temp K	K_{sv}	K_{st}	r^2	τ_0	k_q ($\times 10^8$) s^{-1}
293	4.81	0.35	0.9954	3.99	12.10(3.11)
273	3.84	0.21	0.9997	3.90	9.85(0.85)
253	2.94	0.04	0.9998	3.96	7.42(0.63)
233	2.17	0.20	0.9998	4.13	5.25(0.59)
213	1.16	0.59	0.9996	4.29	2.71(1.12)
193	1.02	0.67	0.9985	4.64	2.20(2.17)
173	0	1.40	0.9975	4.86	0
153	0	1.42	0.9996	5.07	0

Table S-1: Pseudo quenching parameters from fitting of lifetime data for oil 7033 to the modified Stern-Volmer Equation. Errors for the collisional quenching constant are also given in brackets.

Oil	**Emission Wavelength (nm)**	$\triangle H^{\ddagger}$ **kJmol^{-1}**	$\triangle S^{\ddagger}$ **JK^{-1}mol^{-1}**
7033	450	-0.3	-58.2
	500	-0.5	-67.3
	540	-1.3	-75.6
7033 (1:10 dilution)	450	-0.8	-83.5
	500	-0.9	-85.3
	640	-1.32	-90.6
7033 (1:100 dilution)	440	-0.97	-85.1
	500	-0.9	-86.2
	640	-1.3	-91.6
7130	450	-1.2	-76.5
	500	-1.5	-80.6
	530	-3.4	-91.7
7130 (1:10 dilution)	440	-0.6	-89
	500	-0.6	-89.5
	640	-1.1	-94.1
7130 (1:10 dilution)	440	-1.2	-94.7
	500	-1.2	-95.6
	640	-1.3	-96.2
7186	430	-1.5	-91.5
	500	-1.3	-93.5
	530	-1.3	-94.0
7062	440	-1.3	-85.0
	500	-1.6	-89.1
	530	-1.5	-89.5
7197	430	-0.9	-88.8
	500	-1.2	-93.6
	520	-1.0	-92.9

Table S-2: Thermodynamic parameters for some neat and diluted crude oils recovered from fitting lifetime data to the Eyring equation. Fitting was performed using data at temperatures below 213 K. For lighter oils, the data is calculated from the linear part of the Eyring plot (i.e. the lowest temperature region).

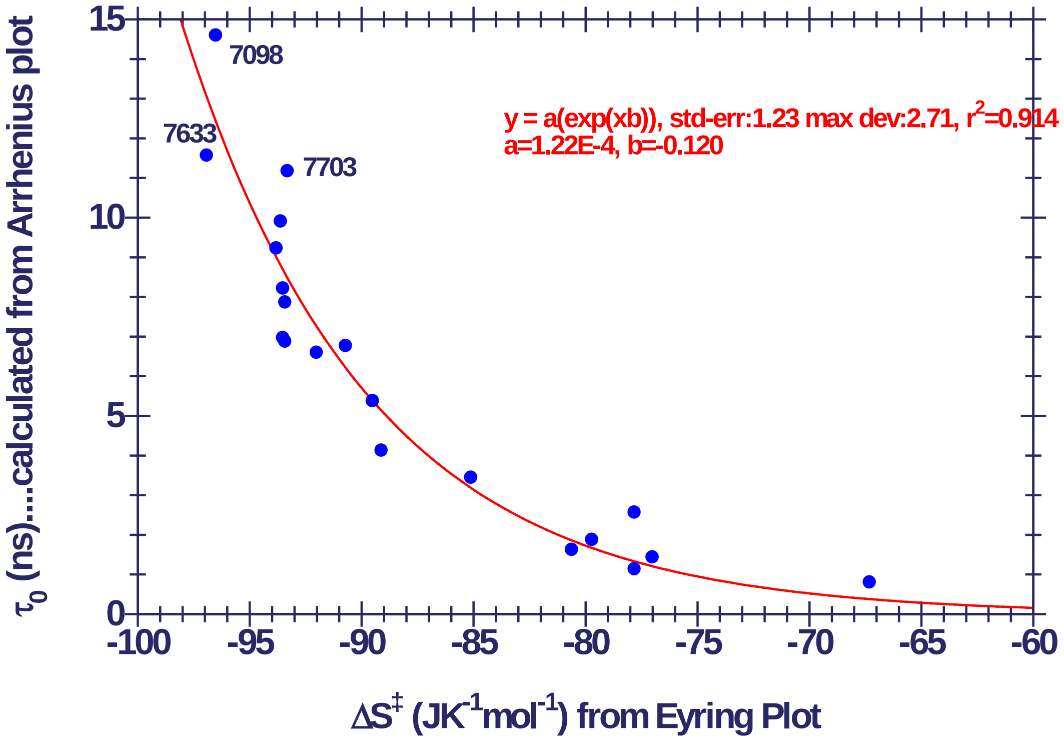

Figure S-6: Scatter plot showing correlation between τ_0 calculated from the Arrhenius equation and entropy calculated from the Eyring model fits for the neat crude oils.

References:

(1) Owens, P.; Ryder, A.; Blamey, N. *J. Fluoresc.* **2008**, *18*, 997-1006.

(2) Ryder, A. G. *Appl. Spectrosc.* **2004**, *58*, 613-623.

(3) Ryder, A. G.; Przyjalgowski, M. A.; Feely, M.; Szuczpak, B.; Glynn, T. *Appl. Spectrosc.* **2004**, *58*, 1106-1115.