Supplementary Information (SI) for Environmental Science: Processes & Impacts.

Supporting Information

Physicochemical properties of tire-derived *para*-phenylenediamine quinones - A comparison of experimental and computational approaches

Simon H. Maguire,[a] Misha Zvekic, [a,b] Angelina Jaeger,[a,b] Joseph Monaghan,[a,b] Erik T. Krogh,[a,b] and Heather A. Wiebe [a,b]

[a] Department of Chemistry, Vancouver Island University, 900 Fifth Street, Nanaimo BC
[b] Department of Chemistry, University of Victoria, 3800 Finnerty Rd, Victoria, BC

Tables S1 – S4

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Equations Eq S1 – Eq S3

Table S1. MS settings and MS/MS transitions for the PerkinElmer QSight 220 ESI-MS/MS † and Thermo Fisher Vanquish HPLC-MS/MS ††.

Analyte	SMILES code	$[M+H]^+$ → Fragment SRM *m/z* transitions	Entrance Voltage (V)	CC L2 (V)	Collision cell (V)
$^{13}C_6$-6PPDQ	CC(C)CC(C)Nc1cc(=O)c(cc1=O)NC1C=CC=CC=1	305 → 221	10	-56	-25
6PPDQ	CC(C)CC(C)Nc1cc(=O)c(cc1=O)NC1C=CC=CC=1	299 → 256	12	-56	-30
DTPDQ	CC1=CC=CC=C1Nc1cc(=O)c(cc1=O)NC1=CC=CC=C1C	319 → 212	10	-84	-31
DPPDQ	O=c1cc(NC2C=CC=CC=2)c(=O)cc1NC1C=CC=CC=1	291 → 263	19	-52	-32
IPPDQ	CC(C)Nc1cc(=O)c(cc1=O)NC1C=CC=CC=1	257 → 215	15	-60	-23
CPPDQ	O=c1cc(NC2CCCCC2)c(=O)cc1NC1C=CC=CC=1	297 → 215	19	-64	-26
77PDQ	CC(C)CCC(C)Nc1cc(=O)c(cc1=O)NC(C)CCC(C)C	335 → 237	25	-92	-26

† Mass spectrometer parameters for the PerkinElmer QSight 220: Positive ion spray voltage: +4.0 kV, hot-surface induced desolvation (HSAID) source: 320 °C, nebulization gas: 120 psi.

†† Mass spectrometer parameters for the Thermo Fisher Vanquish: capillary voltage: +4 kV, ion transfer tube temperature: 300 °C, sheath gas flow: 5 arbitrary units (au), auxiliary gas: 2 au.

Table S2. The experimental conditions and the calculated solubilities and their associated errors for solubility experiments performed using an on-line, CP-MIMS approach.

Compound	Stock Solvent	Final Co-Solvent Concentration (v/v)	Temperature (°C)	Experimental Replicates (*n*)	Solubility(µg L^{-1})	Error Estimate (± µg L^{-1})
6PPDQ	ACN	<1.5%	11	3	29	4
6PPDQ	ACN	<1%	25	3	31	5
6PPDQ	ACN	<2%	41	3	42	6
IPPDQ	MeOH	<0.5%	25	1	106	6
CPPDQ	MeOH	<0.5%	25	1	32	3
77PDQ	MeOH	<0.5%	25	1	6.1	0.8
DTPDQ	MeOH	<0.5%	25	1	3.2	0.3
6PPDQ	ACN	>3% (2% MeOH/DI mixture to start)	25	1	31	4

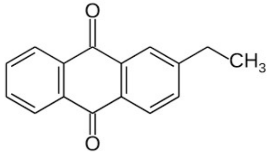
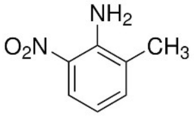
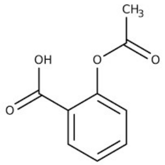
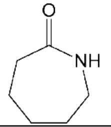
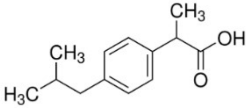
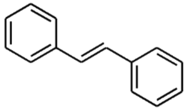
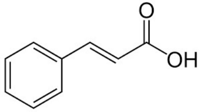
* Error estimates are either based on experimental replicates (n = 3) or data processing (m = 6), the larger error of the two is expressed.

Table S3. Isocratic HPLC-MS chromatogram retention times.

Compound	Isocratic HPLC-MS Retention Time (min)
IPPDQ	1.99
DPPDQ	2.37
CPPDQ	2.80
6PPDQ	2.87
DTPDQ	2.67
77PDQ	16.37*

*Average retention time of two peaks (possible diastereomers).

Table S4: Numerical results for the comparison of calculated log K_{AW} values against experimental log K_{AW} values from Abraham *et al.* 2019.[1] These compounds are not PPDQs, but were chosen as test compounds due to their structural similarity to the PPDQs.

Molecule (CAS Number)	SMILES code	Structure	Abraham *et al.*	DFT	EPI Suite	OPERA
2-ethylanthraquinone (84-51-5)	CCC1=CC2=C(C=C1)C(=O)C3=CC=CC=C3C2=O		-4.81	-4.75	-6.72	-5.05
2-methyl-6-nitroaniline (570-24-1)	CC1=C(C(=CC=C1)[N+](=O)[O-])N		-5.06	-4.67	-5.13	-5.44
Acetylsalicylic acid (50-78-2)	O=C(C)Oc1ccccc1C(=O)O		-8.57	-9.59	-7.28	-6.94
Caprolactam (105-60-2)	O=C1NCCCCC1		-7.98	-7.86	-5.99	-5.71
Ibuprofen (15687-27-1)	CC(Cc1ccc(cc1)C(C(=O)O)C)C		-5.70	-4.33	-5.21	-5.22
trans-stilbene (103-30-0)	c1ccc(cc1)\C=C\c2ccccc2		-2.42	-3.02	-1.53	-1.67
trans-cinnamic acid (140-10-3)	O=C(O)\C=C\c1ccccc1		-6.14	-6.22	-6.16	-5.71

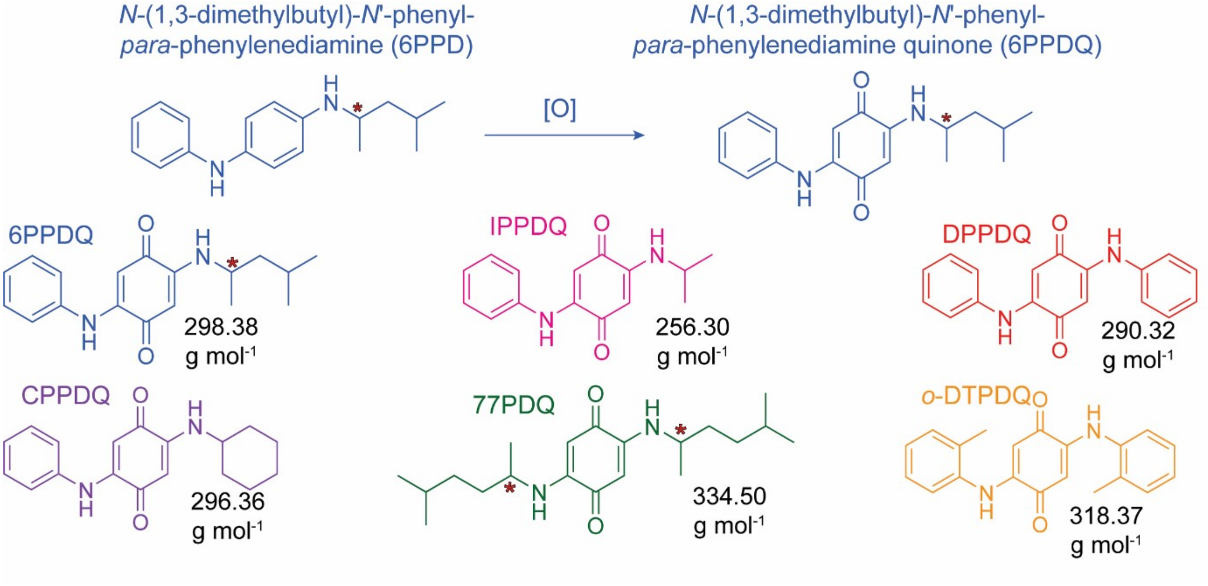


Figure S1. Chemical structures for PPDQs. Chiral centres are indicated with an asterisk.

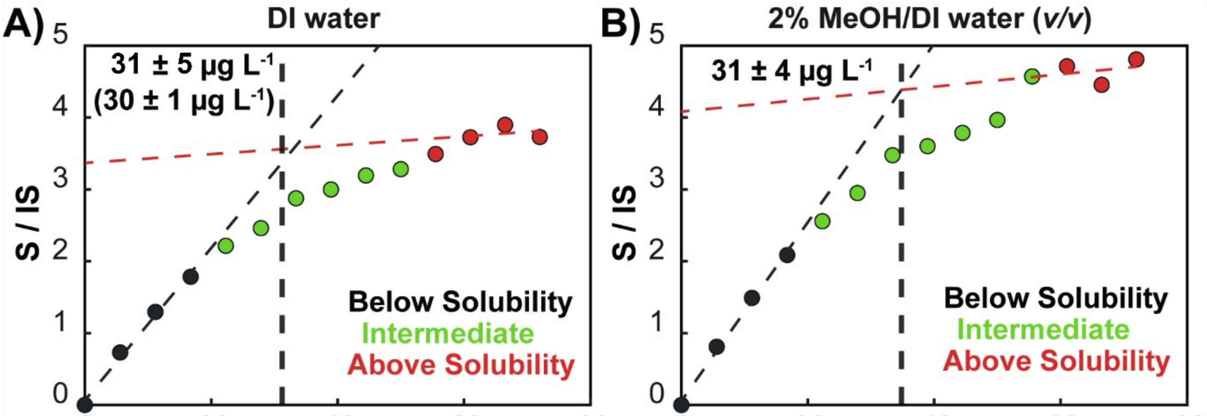


Figure S2. Comparison of 6PPDQ solubility in A) starting solution of deionized water with average and standard deviation based on fit (*m* = 6). Average and standard deviation of experimental replicates (*n* = 3) are included in brackets and B) starting solution of deionized water with 2% methanol co-solvent (*n* = 1) uncertainty based on fit (*m* = 6).

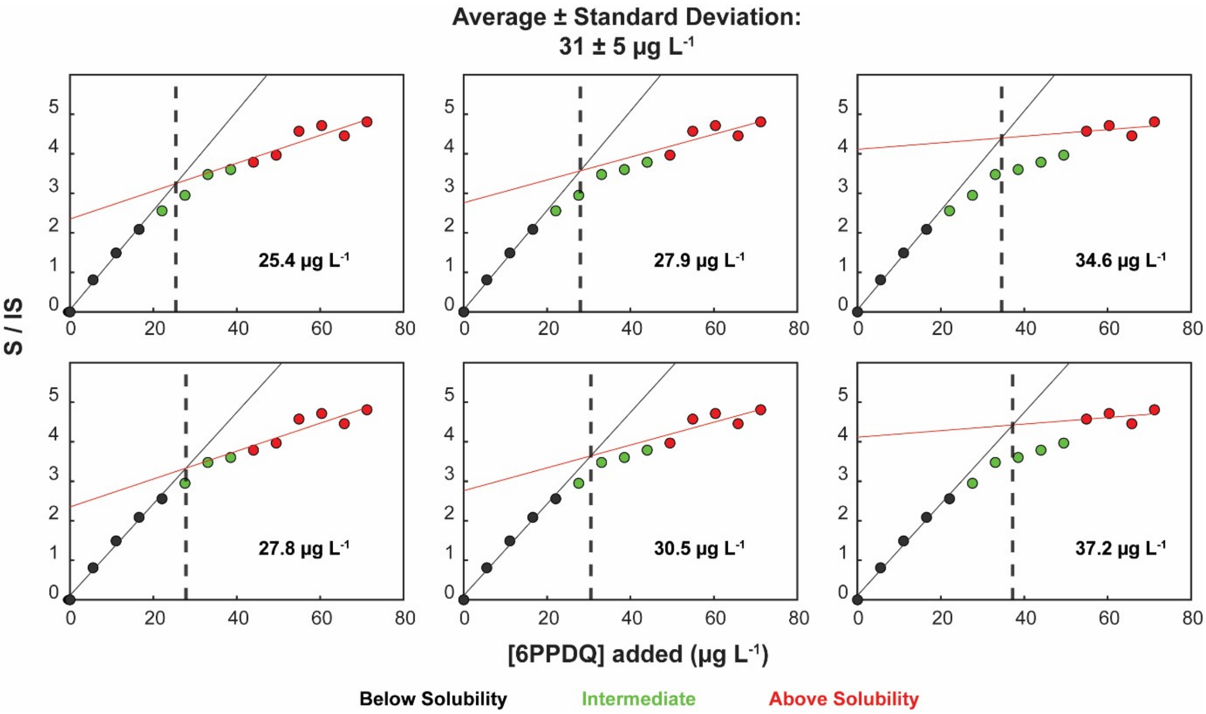


Figure S3. Estimating uncertainty in experimental solubility of 6PPDQ at 25.4 ± 0.2 °C resulting from choosing different data points to generate line fits. We report the mean and standard deviation of six fitting options.

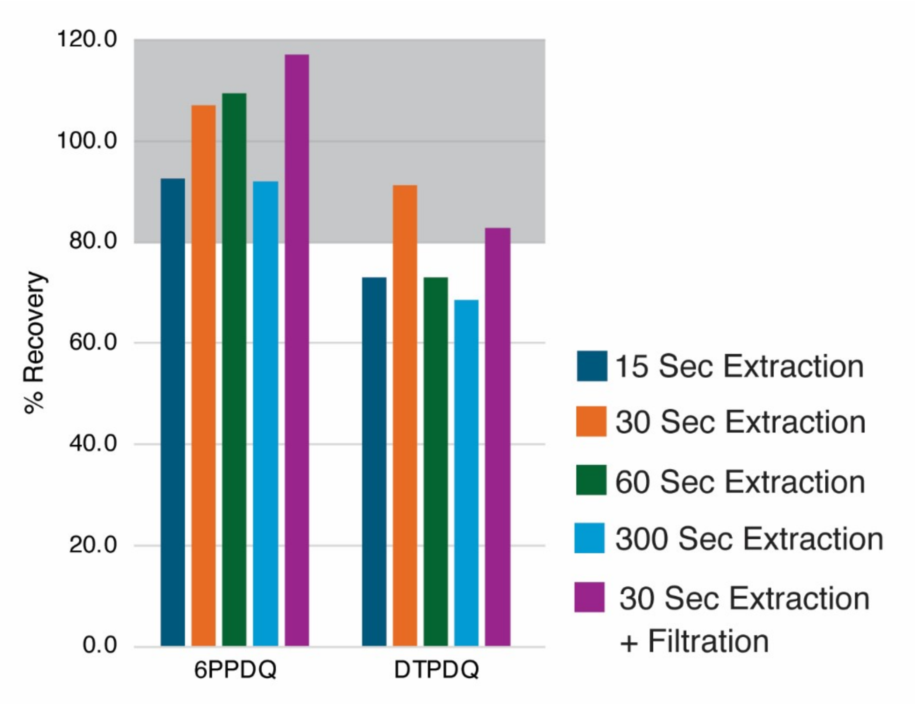


Figure S4. Liquid-liquid extraction recovery for LC-MS solubility analysis. Varied extraction times (heptane-aqueous solution mixing) were tested for optimal extraction efficiency. 30 second extraction was used for solubility work. Internal standard 6PPDQ-d_5 was used for quantitative correction in all experiments.

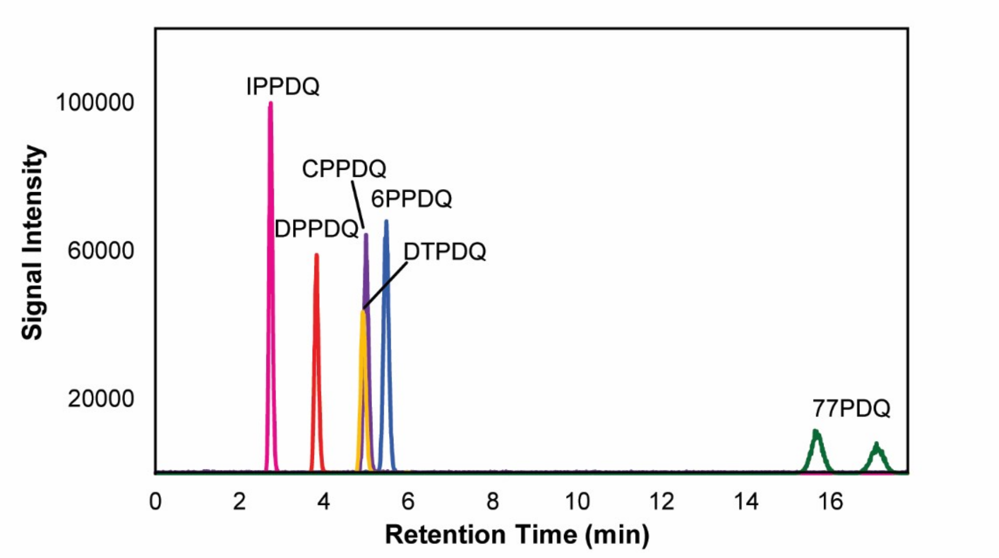


Figure S5. Chromatogram of combined PPDQ standard, isocratic HPLC-MS run of 25/75% water/methanol (*v/v*) with 0.1% formic acid. Under these conditions, the 77PDQ standard analyzed resolved into two peaks under isocratic conditions, potentially due to the presence of diastereomers in the supplied analytical standard.

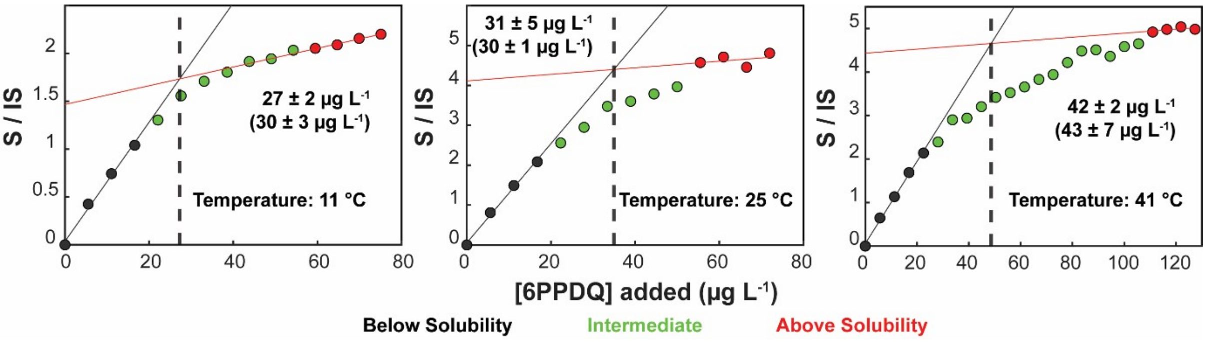


Figure S6. Representative plots of 6PPDQ solubility at varying temperatures via CP-MIMS. Averaged and standard deviation of *n*=3 replicates for the three temperature conditions included in brackets.

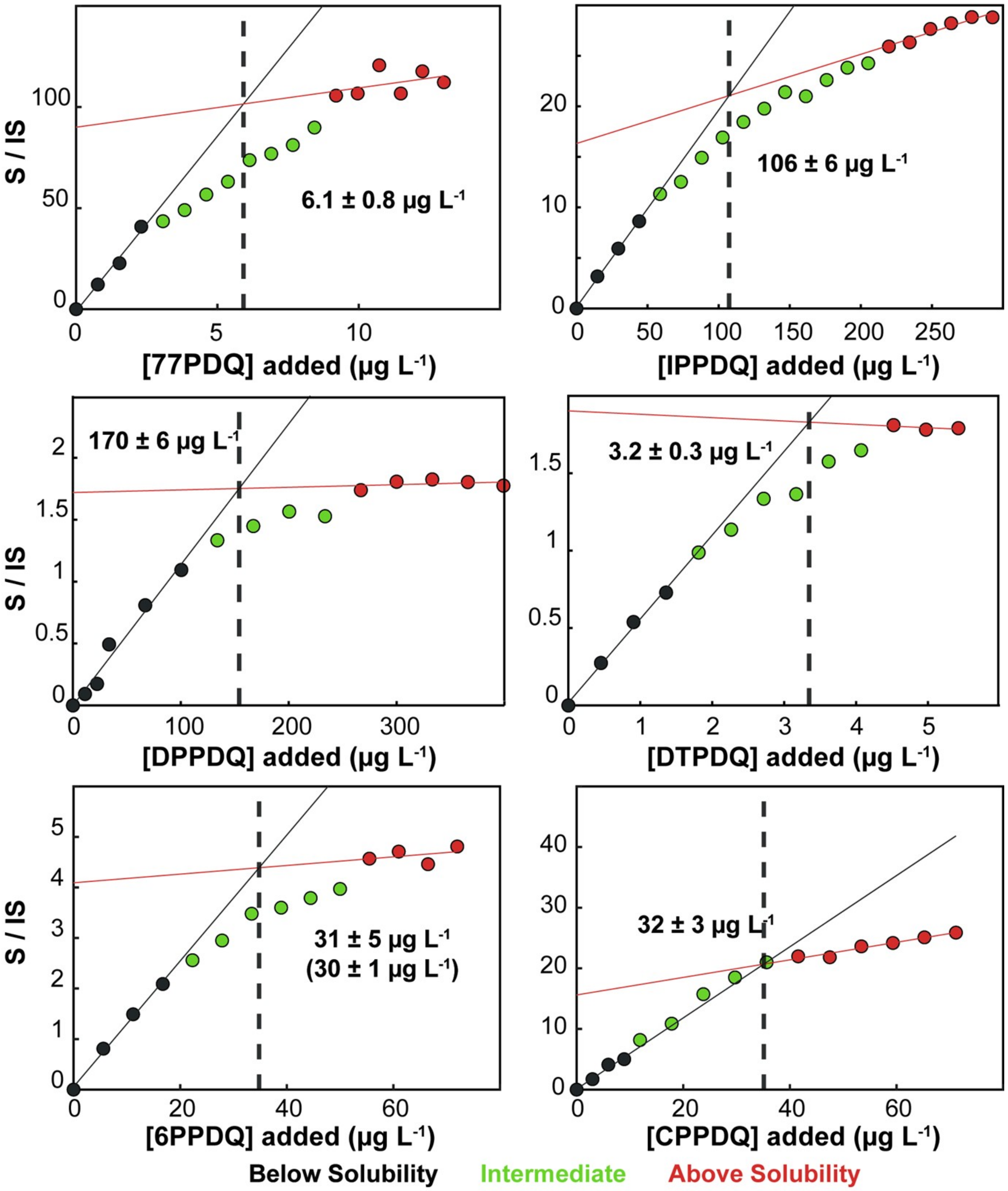


Figure S7. Sample results of normalized signal response for each PPDQ analog compounds at concentrations below (black data), above (red data), and at intermediate (green data) solubility. Experiments were done at 25 °C.

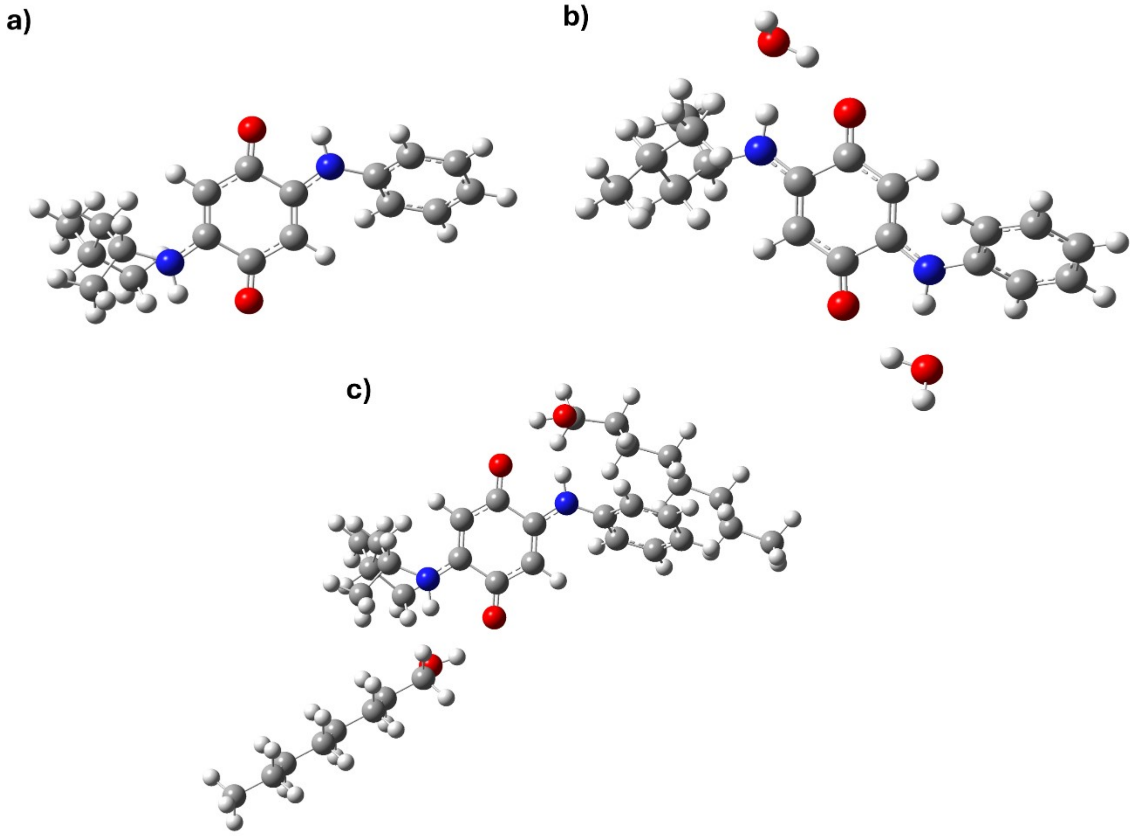


Figure S8. DFT-optimized geometries for 6PPDQ a) in the gas phase, b) bound to two explicit water molecules and c) bound to two explicit *n*-octanol molecules.

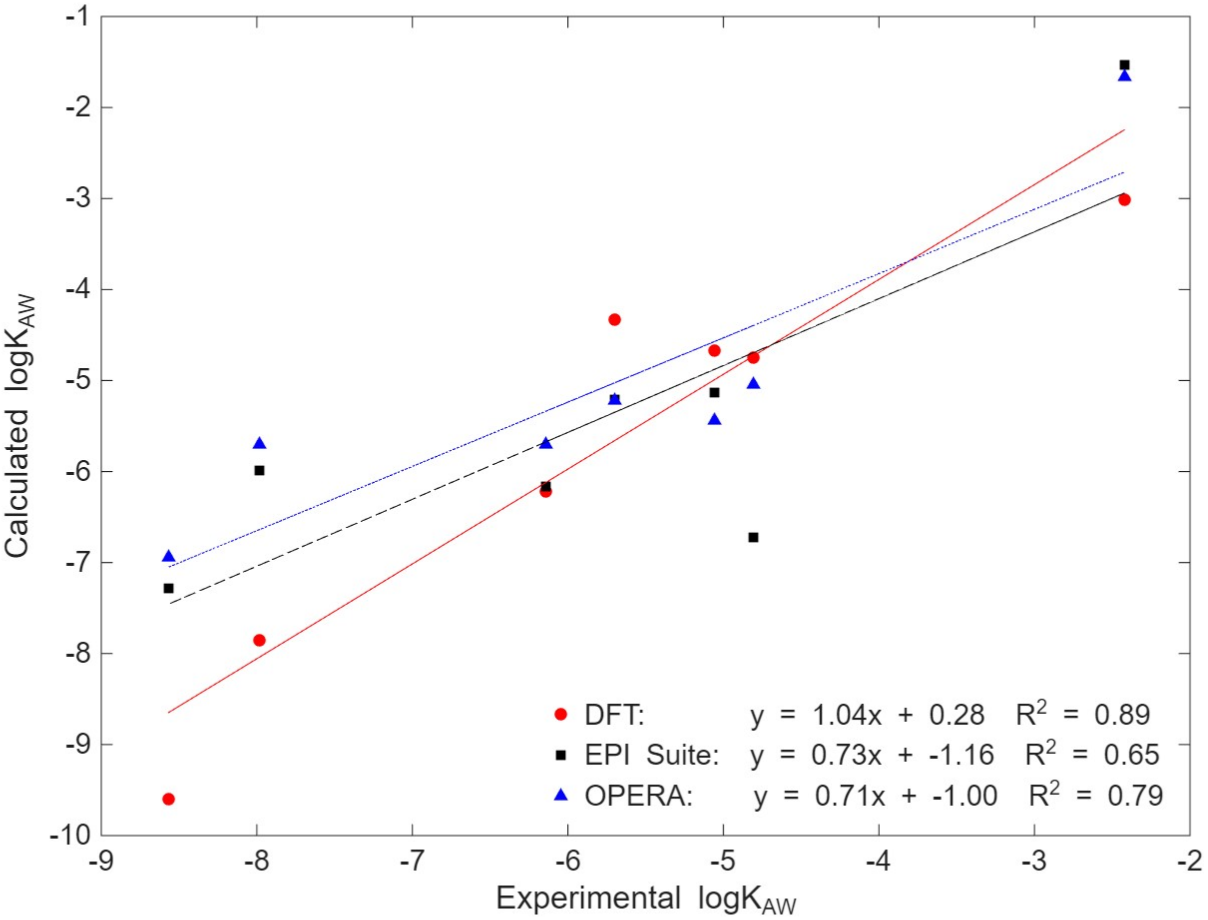


Figure S9. Comparison of DFT,EPI Suite and OPERA calculated log K_{AW} against experimental log K_{AW} from Table S4. The DFT calculated logK_{AW} are in better agreement with the experimental data than the QSARS methods.

Equation S1. Conversion of Henry's law constants to unitless K_{AW} values.

$$K_{AW} = \frac{K_H}{RT}$$

where R is the ideal gas constant (8.314 $Pa \cdot m^3 \cdot mol^{-1} \cdot K^{-1}$ or 8.206×10^{-5} atm L mol^{-1} K^{-1}) and T is 298 K.

Equation S2. General equation from WSKOWWIN to estimate water solubility for any molecule from log K_{OW}.

$$log\ S = 0.796\ - 0.854\ [KOWWIN\ log\ K_{ow}] - 0.00728\ MW + C$$

where log *S* is the predicted log water solubility in mol/L, log K_{OW} is the unitless log octanol-water partition ratio calculated by KOWWIN, MW is the molecular weight in g/mol, and *C* is a unitless correction factor. For compounds with aliphatic amines (such as PPDQs), WSKOWWIN uses C = 1.008 by default.

Equation S3. Calculation of re-calibrated correction factor for PPDQ water solubility

$$C' = log\ S - 0.796 + 0.854\ [\mathrm{KOWWIN\ 6PPDQ\ log}\ K_{ow}] + 0.00728\ MW$$

Rearranging equation S2 yields an expression for the re-calibrated correction factor for the PPDQs. Here, log S is the experimentally-determined log water solubility for 6PPDQ from this work, log Kow is the KOWWIN-predicted unitless partition ratio for 6PPDQ, and MW is the molar weight of 6PPDQ

We calculate C' using equation S3 to be -2.207. Corrected water solubilities for the different PPDQs are calculated by using C' in the place of C in equation S2 and appear in Table 1 of the main text.

References:

1. Abraham, M. H.; Acree, W. E.; Hoekman, D.; Leo, A. J.; Medlin, M. L. A New Method for the Determination of Henry's Law Constants (Air-Water-Partition Coefficients). *Fluid Phase Equilibria* **2019**, *502*, 112300. https://doi.org/10.1016/j.fluid.2019.112300.