Supplementary Materials

for

Analysis of polycyclic aromatic hydrocarbons in water samples using deep eutectic solvent as a dispersant in dispersive liquid–liquid microextraction based on the solidification of floating organic droplet

Chunlong Peng [1], Jinfeng Hu [1] and Xin Li [2, 3]*

[1] Institute of Natural Medicine and Health Products, School of Pharmaceutical Sciences, Zhejiang Provincial Key Laboratory of Plant Ecology and Conservation, Taizhou University, Taizhou 318000, China; pengcl@tzc.edu.cn (C.Z.); jhhu@fudan.edu.cn (J.H.)

[2] Zhejiang Provincial Key Laboratory of Plant Evolutionary Ecology and Conservation, Taizhou University, Taizhou 318000, China

[3] School of Food and Engineering, Shaanxi University of Science and Technology, Xi'an 710021, China

* Correspondence: lixin2013@tzc.edu.cn; Tel.: +86-152-6766-6103

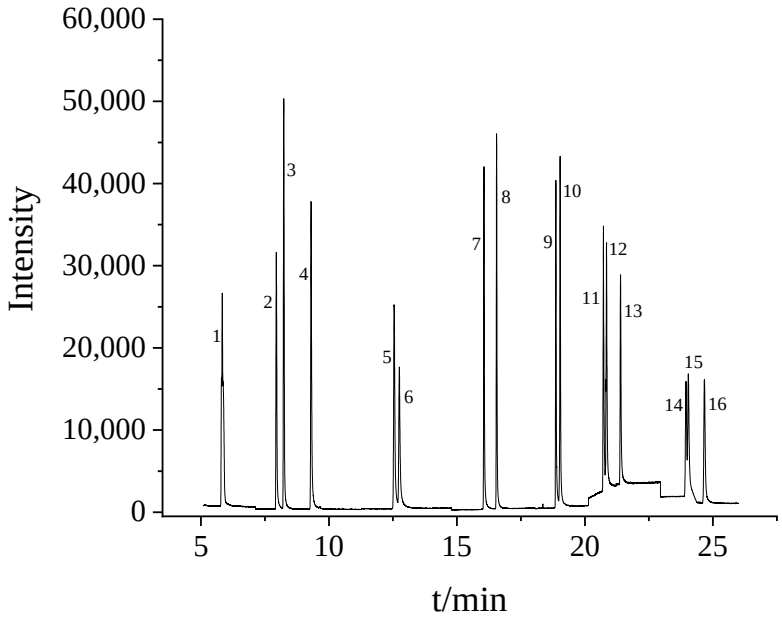


Figure S1. Chromatogram of the 16 PAHs obtained for a 100 ng/L standard mixture. Peaks: 1) Naphthalene, 2) Acenaphthylene, 3) Acenaphthene, 4) Fluorene, 5) Phenanthrene, 6) Anthracene, 7) Fluoranthene, 8) Pyrene, 9) Benz[a]anthracene, 10) Chrysene, 11) enzo[b]fluoranthene, 12) Benzo[k]fluoranthene, 13) Benzo[a]pyrene, 14) Indeno[1,2,3-c,d]pyrene, 15) Dibenz[a,h]anthracene, 16) Benzo[g,h,i]perylene

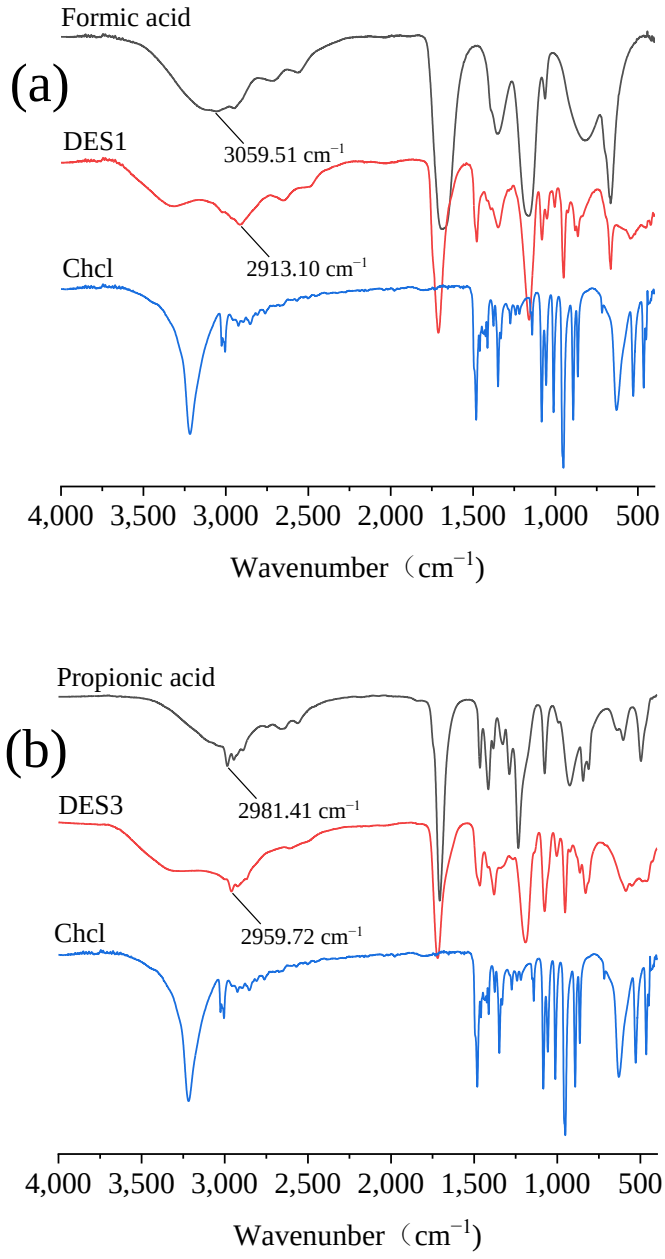


Figure S2. (**a**) FT-IR spectra of formic acid, ChCl and DES1, and (**b**) the FT-IR spectra of propionic acid, ChCl and DES3.

As shown in Figure S2, compared with those of formic acid (3059.51 cm^{-1}) and propionic acid (2981.41 cm^{-1}), the O-H stretching vibration peaks of DES1 and DES3 shifted to lower wave numbers 2913.10 cm^{-1} and 2959.72 cm^{-1}, respectively. These may be due to the transfer of oxygen atom's electron cloud to hydrogen bonding and consequently a decrease in the absorption peak. Accordingly, the shift of O-H stretching vibration peak indicated the existence of hydrogen bonding between their components when both DES1 and DES3 were formed.

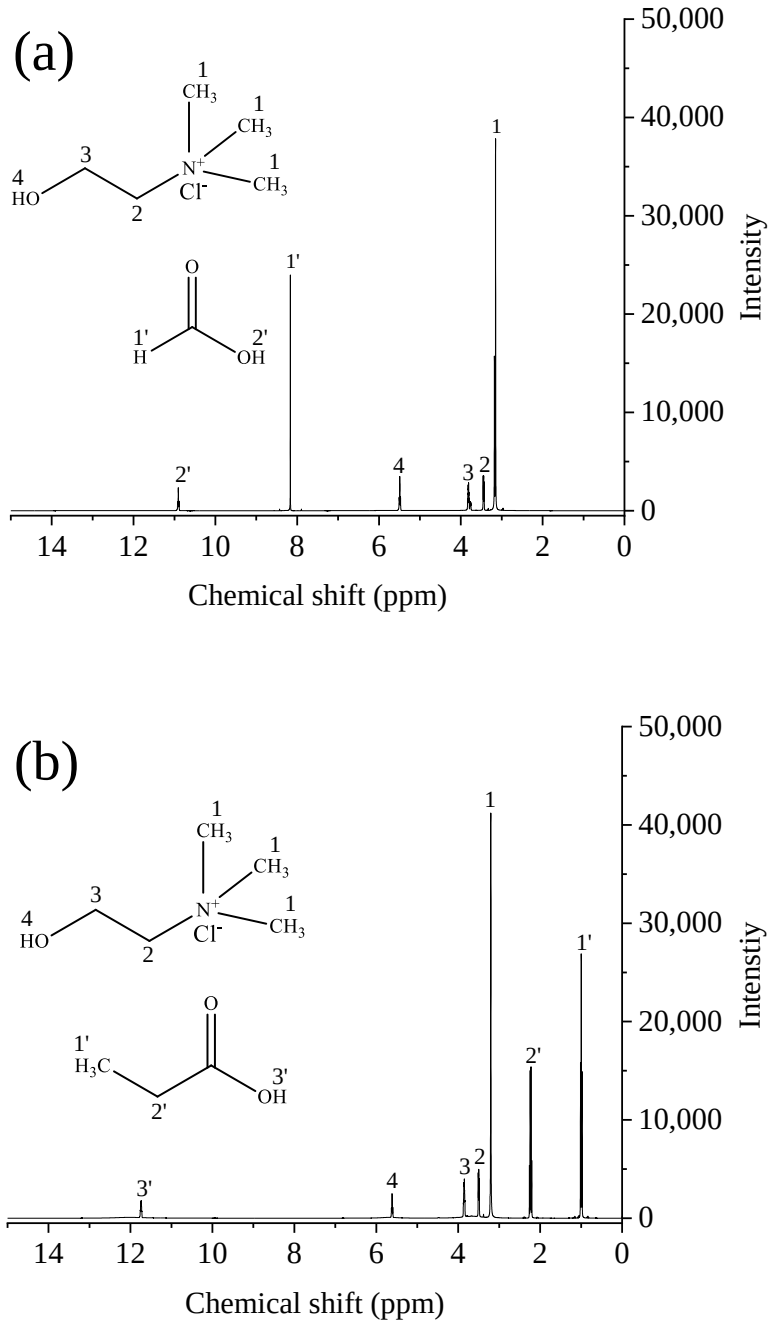


Figure S3. ^{1}H NMR spectra of (**a**) DES1 and (**b**) DES3.

As shown in Figure S3, all peaks of DES1 can be assigned to ChCl and formic acid, and all peaks of DES3 can be assigned to ChCl and propionic acid, suggesting that no side reactions are present during the syntheses of DES1 and DES3. Thus, the ^{1}H NMR spectra indicated that both the formation of DES1 and DES3 were formed between the hydroxyl groups.

Table S1. The peak area value of each PAH in Figure 3.

PAH	Average peak area (n=3)			PAH	Average peak area (n=3)		
	1-decanol	1-undecanol	1-dedecanol		1-decanol	1-undecanol	1-dedecanol
Naphthalene	47,733	53,112	62,469	Benz[a]anthracene	49,521	54,009	66,288
Acenaphthylene	43,885	49,415	62,218	Chrysene	60,996	68,851	80,731
Acenaphthene	66,931	77,181	91,465	Benzo[b]fluoranthene	51,159	55,921	67,583
Fluorene	59,761	66,541	79,694	Benzo[k]fluoranthene	51,050	58,515	70,530
Phenanthrene	51,852	58,288	69,249	Benzo[a]pyrene	38,477	42,686	51,233
Anthracene	43,308	48,615	60,650	Indeno[1,2,3-c,d]pyrene	35,037	38,559	45,735
Fluoranthene	57,525	62,857	76,482	Dibenz[a,h]anthracene	36,989	40,095	47,816
Pyrene	68,135	75,182	90,746	Benzo[g,h,i]perylene	37,062	41,868	51,742

Table S2. The peak area value of each PAH in Figure 4.

PAH	Average peak area (n=3)					
	DES1	DES2	Methanol	Ethanol	Acetonitrile	Acetone
Naphthalene	61,320	72,755	54,927	52,632	63,097	57,966
Acenaphthylene	58,800	67,692	52,635	48,941	58,949	55,244
Acenaphthene	89,849	10,5726	79,870	75,924	90,894	85,508
Fluorene	76,620	91,152	68,886	64,552	78,658	72,774
Phenanthrene	69,147	79,846	61,543	58,227	70,026	66,313
Anthracene	55,826	66,595	49,854	47,701	57,758	51,970
Fluoranthene	74,272	86,104	66,821	62,687	75,050	70,154
Pyrene	87,900	102,988	79,538	73,334	89,311	84,058
Benz[a]anthracene	63,798	73,984	57,341	53,102	64,948	59,444
Chrysene	80,588	94,316	71,015	67,714	81,796	76,444
Benzo[b]fluoranthene	65,451	76,604	59,096	55,687	67,355	63,138
Benzo[k]fluoranthene	68,691	80,157	60,793	57,583	70,305	64,104
Benzo[a]pyrene	49,770	58,473	44,154	42,98	51,138	47,824
Indeno[1,2,3-c,d]pyrene	45,385	52,820	40,181	38,389	45,987	42,178
Dibenz[a,h]anthracene	46,870	54,925	42,015	40,249	48,151	45,541
Benzo[g,h,i]perylene	49,392	57,352	43,869	41,990	49,858	46,548