Electronic Supplementary Information: QSAR aided design and development of biopolymer-based SPE phase for liquid chromatographic analysis of polycyclic aromatic hydrocarbons in environmental water samples

ESI 1. Data treatment for DFT computational study

Quantum chemical descriptors such as ionization potential (I), electron affinity (A), and energy gap (ΔE) were respectively calculated according to equations 3.1 – 3.7

$$I = -E_{HOMO} \quad (1)$$

$$A = -E_{LUMO} \quad (2)$$

$$\Delta E = E_{HOMO} - E_{LUMO} \quad (3)$$

where E_{LUMO} and E_{HOMO} are the energies of Lowest Unoccupied Molecular Orbitals and Highest Occupied Molecular Orbitals respectively, generated from the DFT calculations.

ESI 2. Evaluation of method performance and validation

2.1 Method Detection Limit

To evaluate the method detection limits, the official method of the US EPA [22] was applied. Method detection limit, MDL was calculated by the following expression:

$$MDL = t \times s \qquad 1$$

where t is the Student's t value for a 99% confidence interval and a standard deviation estimate with n–1 degrees of freedom, and s is the standard deviation of the replicate analyses.

For this study, six replicate analysis of laboratory tap water samples (isotope preparatory lab of centre for environmental remediation, IGSNRR, Beijing) were done. The spike level for the tap water was 0.5 for fluorescence detector, and 1.0 and 10 µg/L for UV detector.

2.2 Precision

The precision was measured as the relative standard deviations (RSD) of the data obtained from the experiment for method detection limit. RSD was calculated using the following expression:

$$RSD = \frac{s}{\bar{x}} \times \frac{100}{1} \qquad 2$$

where s is the standard deviation, and $\bar{x}$ is the mean value of the six replicate measurements.

2.3 Linearity and Linear range of the method

For this study, the water samples containing 0.5, 5.0, 25.0, and 50.0 µg/L of US EPA PAH mix were prepared, preconcentrated and analyzed. The peak response (peak area) was plotted

against the corresponding concentration value. The linearity was assessed as r^2 values of the straight line plots.

2.4 Recovery study

The water samples used for the recovery studies were tap water collected from isotope preparatory lab of centre for environmental remediation, IGSNRR, Beijing, and polluted water samples collected from Shahe river (40°7'43.36"N, 116°19'9.43"E), Beijing. The recovery study was done by analyzing the un-spiked and spiked water samples, and the percentage recovery was calculated as follows:

$$\text{Recovery} = \frac{C_{SP} - C_{UP}}{SL} \times \frac{100\%}{1} \qquad 3$$

where C_{SP} is the concentration of the spiked sample, C_{UP} is the concentration of the unspiked sample, and SL is the spike level.

For the recovery study, the spike level for both tap and Shahe river samples was 10 μg/L. The optimum values of the SPE parameters as determined from the optimization experiments were applied for the recovery study.

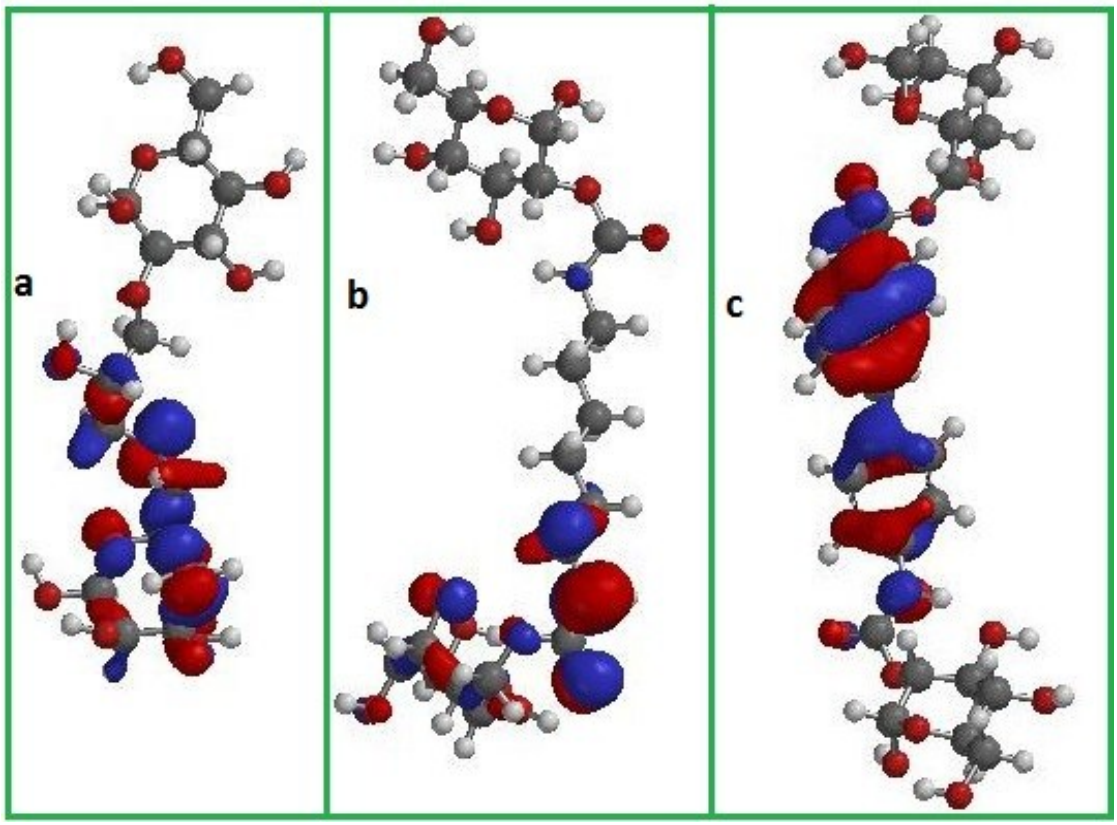

Figure S1: Highest occupied molecular orbital (HOMO) of (a) EPI biopolymer (b) HDI biopolymer and (c) MDI biopolymer[12]

Table ESI. 1. Excitation and emission wavelength for fluorescence detection

Constituent PAHs	Excitation wavelength	Emission wavelength
Naphthalene	224	330
Acenaphthylene	not detected	
Acenaphthene	234	320
Fluorene	224	320
Phenanthrene	224	320
Anthracene	250	370
Fluoranthene	252	402
Pyrene	238	398
Benzo (a) anthracene	238	398
Chrysene	238	398
Benzo(b)fluoranthene	268	398
Benzo(k)fluoranthene	268	398
Benzo(a)pyrene	268	398
Dibenzo(a,h)anthracene	234	420
Benzo(g,h,i)perylene	234	420
Indeno(1,2,3-cd)pyrene	300	466