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Capturing polycyclic aromatic sulfur heterocycles in electron donor–acceptor complexes

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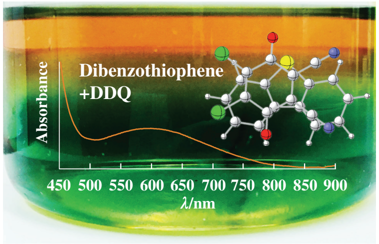
Stoichiometry and stability of electron donor–acceptor complexes formed by dibenzothiophene and its alkylated derivatives with DDQ and TCNE in nonpolar organic solvents has been investigated. 4,6-Dimethyldibenzothiophene produces the most stable 1 : 1 complex with DDQ in agreement with energy levels of the π-donors HOMOs and π-acceptors LUMOs calculated by DFT. The results make possible an employment of the complexes for multiplex determination of polycyclic aromatic pollutants using surface enhanced Raman spectroscopy.



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Selective detection and sensitive determination of polycyclic aromatic hydrocarbons (PAHs) are of particular interest, since they represent hazardous environmental pollutants and quality markers of petroleum products.[1,2] Along with PAHs, polyaromatic sulfur heterocycles (PASHs) are persistent contaminants as a result of oil processing[3] and spills.[4,5] The relative abundance of dibenzothiophene (DBT), 4-methyldibenzothiophene (4MDBT), 4,6-dimethyldibenzothiophene (46DMDBT), 4,6-diethyldibenzothiophene (46DEDBT) and other similar PASHs represent a chemical fingerprint of a crude oil. Consequently, they constitute reliable features for distinguishing the oil signatures during spill events[6] and should be considered as oil quality markers as well as the markers of pollution in wastewater.[7]

Modern standards for the content of sulfur compounds in fuels lead to the necessity to create and introduce the methods for multiplex sensitive determination of PAHs/PASHs as well as their monitoring in hydrocarbon raw materials and refined oil products, such as HPLC for determination of PASHs in water samples[8,9] or gas chromatography for oil fuel samples.[10] However, these well-established techniques are not portable, rather time-consuming, require expensive and bulk equipment, sample pretreatment as well as qualified personnel.

Most of the above drawbacks of chromatographic methods can be overcome *via* employment of surface enhanced Raman spectroscopy (SERS),[11] which represents a quite young and promising analysis technique, though insufficiently explored for practical applications.[12,13] The Raman signal can be amplified by a factor of 10^{10}–10^{12} due to the effect of surface plasmon resonance (SPR) on the nanostructured surface of noble metals, which opens up new avenues for lowering detection limits for a broad range of analytes.[14] However, the use of SERS for determination of the quality markers of petroleum products is very limited[15] because of (i) the absence in PAHs/PASHs of any functional groups able to anchor the noble metals; (ii) the absence of visible light absorption for DBTs [Figure 1(*a*)], while the SPR band of silver nanoparticles lies at ~420 nm and (iii) prohibition of additional resonant surface enhancement with typically utilized monochromatic laser radiation, *e.g.*, 514.5 and 632.8 nm.[16,17]

To make possible the use of SERS for the above purposes, we employed the ability of DBTs to act as effective π-donors in the charge transfer complexes (CTCs) with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) and tetracyanoethylene (TCNE),[18,19] with these complexes absorbing visible light.[20] In this work we investigated the stoichiometry and calculated the stability constants of CTCs for DBT, 4MDBT, 46DMDBT and 46DEDBT in nonpolar solvents. These complexes can be further employed as new indicator systems for the determination of PASH quality markers in petroleum products using SERS.[2,21]

Solvent nature has a significant effect on the formation of CTCs. We have established the ability of hexane, chloroform, dichloromethane and lower alcohols to redistribute the charge in the donor–acceptor complex in the ground state, which leads to a change in the electronic structure of the complex in its excited state.[22] The modification of the electronic structure, in turn, results in solvation of the donor and acceptor. In the ground state the degree of electron transfer in the complex is small. Therefore, local polar centers of the donor and acceptor affect the solvent molecules stronger than insignificant δ^+ and δ^- charges of the resulting complex.[23–25] It is known that chloroalkanes represent the most suitable solvents for the formation of CTCs from DBTs and chloroform is the optimal one, since the complexes obtained in its medium are characterized by the largest extinction coefficients.[22]

These assumptions about CTCs formation were confirmed by estimation of molecular orbitals for both donors and acceptors using density functional theory (DFT). The calculations were carried out with a Q-Chem 5.2 software.[26] The best description of electron density is typically obtained employing functionals designed in the late 1990s, such as PBE0,[27] so the PBE0 method with 6-311++G(d,p) basis set was used in this work. DDQ[28,29] and TCNE[30,31] have been chosen as commercially available

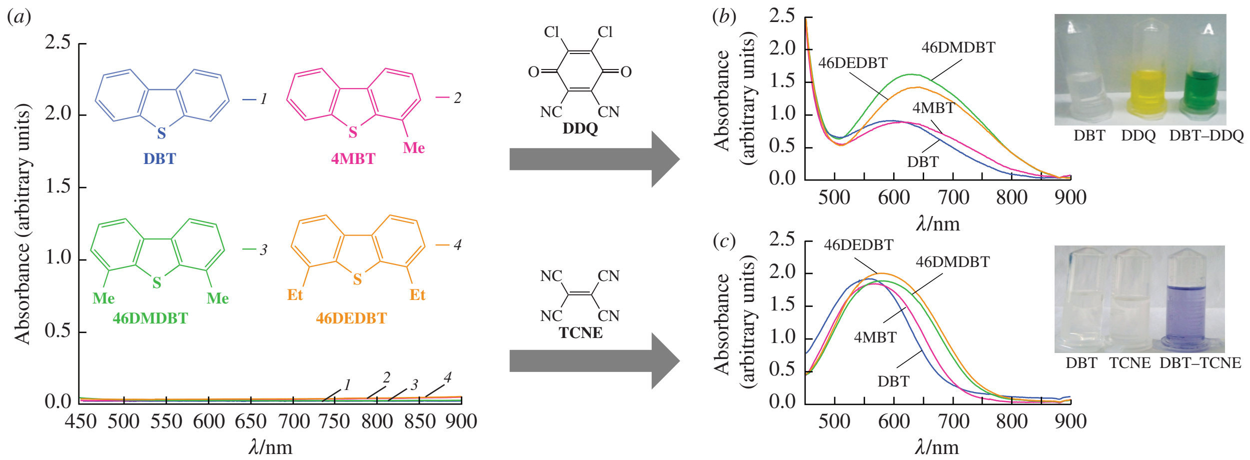

Figure 1 UV-VIS spectra of (*a*) DBT and its derivatives in *n*-heptane as well as the corresponding CTCs (1 : 1 mol) formed in chloroform with (*b*) DDQ and (*c*) TCNE.

electron-deficient compounds with LUMO energy levels –5.33 and –5.06 eV, respectively, which are low enough to make these π-acceptors capable of trapping DBTs in the corresponding CTCs [Figure 2(*a*)]. A solution of DDQ in chloroform has a yellow color ($\lambda_{\max}$ ~400 nm), while TCNE is colorless ($\lambda_{\max}$ ~350 nm) [Figure 1(*b*),(*c*)]. When DBTs were mixed with the π-acceptors, the donor–acceptor complexes formed at once with immediate change of the solution color due to new absorption maxima in UV-VIS spectra of CTCs in the wavelength range of 550–650 nm potentially overlapping with the SPR band of silver[32–34] and gold[35,36] nanoparticles.

The stoichiometry of CTCs was determined by the Bent–French method. It was found to be 1 : 1 for DDQ with DBTs in *n*-heptane, *n*-octane and isooctane as nonpolar solvents representing an oil fuel matrix. However, complexes of TCNE with DBTs in isooctane preferably formed in the following stoichiometries: TCNE–DBT 1 : 1, TCNE–4MDBT 3 : 2 or 4 : 3, TCNE–46DMDBT 5 : 4 and TCNE–46DEDBT 3 : 2 or 4 : 3 (for details, see Online Supplementary Materials). On the contrary, in *n*-heptane the complexes TCNE–DBT, TCNE–4MDBT, TCNE–46DMDBT and TCNE–46DEDBT formed in different stoichiometries, namely 1 : 1, 4 : 3, 4 : 3 or 3 : 2 and 4 : 3, respectively. The larger number of π-acceptor molecules per one donor molecule can be explained by the smaller size of TCNE molecule compared with DBTs and DDQ ones. This inconsistency of stoichiometry depending on the specific analyte and the sample matrix makes TCNE an inappropriate candidate for trapping DBTs and their further quantitative determination using SERS.

Stability constants of the CTCs of DBTs with DDQ were calculated by the Foster–Hammick–Wardley method[37] employing the Benesi–Hildebrand equation.[38] Assuming A for π-acceptor, D for π-donor, DA for their complex and introducing the approximation $[A]_0 \gg [D]_0$, the following expression for the formation constant K_f of the complex

$$K_f = [DA]/([D]\,[A]) \tag{1}$$

can be transformed into an equation suitable for calculating K_f from the experimental data using the following formula:

$$\left.\begin{array}{l} K_f = \dfrac{[DA]}{([D]_0 - [DA])([A]_0 - [DA])} \\ [D]_0 - [DA] \approx [A]_0 \\ \text{Abs} = \varepsilon_{\max}\, l\, [DA] \\ l = 1\text{ cm} \end{array}\right\} \Rightarrow \frac{[D]_0}{\text{Abs}} = \left(\frac{1}{[A]_0}\right)\left(\frac{1}{\varepsilon K_f}\right) + \frac{1}{\varepsilon}, \tag{2}$$

where Abs represents optical density and l is an optical path length. Experimental values of Abs were obtained varying the total concentration of the acceptor at constant concentration of the donors. The complex formation constant K_f was calculated by linearization of the Benesi–Hildebrand equation in the coordinates $x = 1/[A]_0$ and $y = [D]_0/\text{Abs}$. The molar absorption coefficient $\varepsilon_{\max}$ was found as the reciprocal of the segment cut off by the resulting extrapolated graph on the ordinate axis (for details, see Online Supplementary Materials).

The results obtained [Figure 2(*b*)] indicate an increase in the stability of CTCs from DBT to its methylated derivatives, which has been confirmed by the energy levels of HOMO. The diethyl derivative 46DEDBT produced less stable donor–acceptor complex due to steric hindrance from the two ethyl groups [see Figure 2(*b*)].

Due to the fact that the DBTs investigated form stable complexes, it is possible to detect them with high sensitivity using SERS.[21]

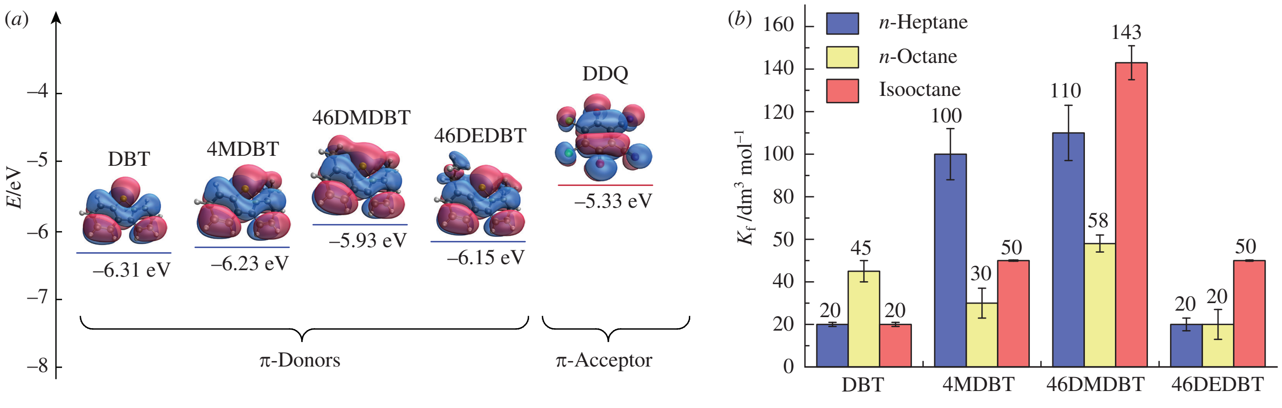

Figure 2 (*a*) DFT-calculated HOMO energy levels of PASHs as π-donors and LUMO energy level of DDQ as a π-acceptor. (*b*) Experimentally determined stability constants for the CTCs formed by DBTs and DDQ in heptane, octane and isooctane.

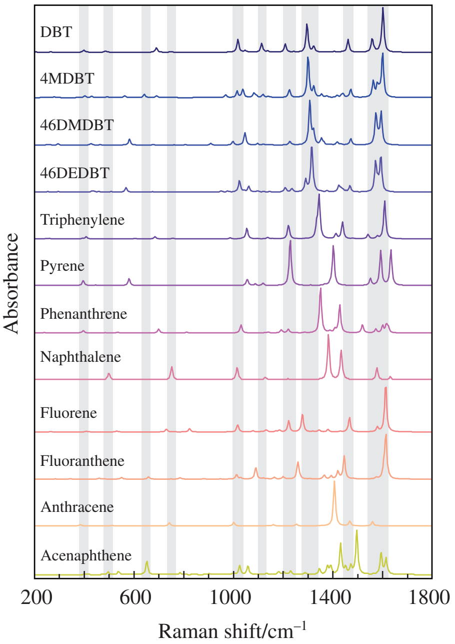

Figure 3 DFT-simulated gas phase Raman spectra of DBTs and PAHs.

However, PAHs like triphenylene, pyrene, phenanthrene, naphthalene, fluorene, fluoranthene, anthracene or acenaphthene, which may be present in the oil fuel at 10^3 times higher concentrations than PASHs, can also act as effective π-donors and thus form stable donor–acceptor complexes with the same π-acceptors.[2] Therefore, it is important to attain additional selectivity and multiplexity of the analysis using the narrowness of Raman bands and unique spectral fingerprints of each detected molecule. DFT-simulated Raman spectra of DBTs and PAHs are shown in Figure 3, where all the calculated Raman cross sections have been convoluted by a Lorentzian function with the half maximum width of 5 cm^{-1} and the empirically chosen scaling factor of 0.96. Unmixing, or deconvolution, of various PAHs in their complex mixture can be achieved by the well-known direct classical least squares (DCLS) demultiplexing.[39] Thus, the binding of PASHs, which represent hazardous sulfur containing contaminants and/or quality markers of petroleum products, into the CTCs opens up an avenue towards determination of DBT and its alkylated derivatives with required sensitivity and selectivity,[2,21] due to realization of the effect of surface enhanced resonant Raman scattering (SERRS).

In summary, stoichiometry and stability constants for electron donor–acceptor complexes of DBTs with DDQ and TCNE have been determined. It was demonstrated that formation of this CTCs resulted in appearance of new absorption bands at 550–650 nm close enough to the SPR bands of silver and gold nanoparticles and the laser wavelengths, *e.g.*, 514.5 and 632.8 nm, typically used in Raman microscopes. This fact allows the determination of various PAHs in oil fuel using SERS.[2,18] The experimentally determined stability constants are in agreement with DFT-calculated energy levels of molecular orbitals and, with consideration of the molecule geometry, can be applied to the prediction of stability for other CTCs.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2021.05.015.

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