# Capturing polycyclic aromatic sulfur heterocycles in electron donor–acceptor complexes

**Olga E. Eremina, Mariia V. Samodelova, Mariia V. Ferree, Tatyana N. Shekhovtsova and Irina A. Veselova**

**Table S1** Maximum wavelength of charge transfer complexes with DDQ in *n*-heptane, *n*-octane, and isooctane

| with DDQ in CHCl$_3$ | $\lambda_{max}$ in *n*-heptane, nm | $\lambda_{max}$ in *n*-octane, nm | $\lambda_{max}$ in isooctane, nm |
|---|---|---|---|
| **Dibenzothiophene** | $590 \pm 10$ | $590 \pm 10$ | $590 \pm 10$ |
| **4MDBT** | $605 \pm 10$ | $605 \pm 10$ | $620 \pm 10$ |
| **46DMDBT** | $610 \pm 10$ | $625 \pm 10$ | $620 \pm 10$ |
| **46DEDBT** | $615 \pm 10$ | $630 \pm 10$ | $640 \pm 10$ |

**Table S2** Maximum wavelength of charge transfer complexes with TCNE in *n*-heptane, *n*-octane, and isooctane

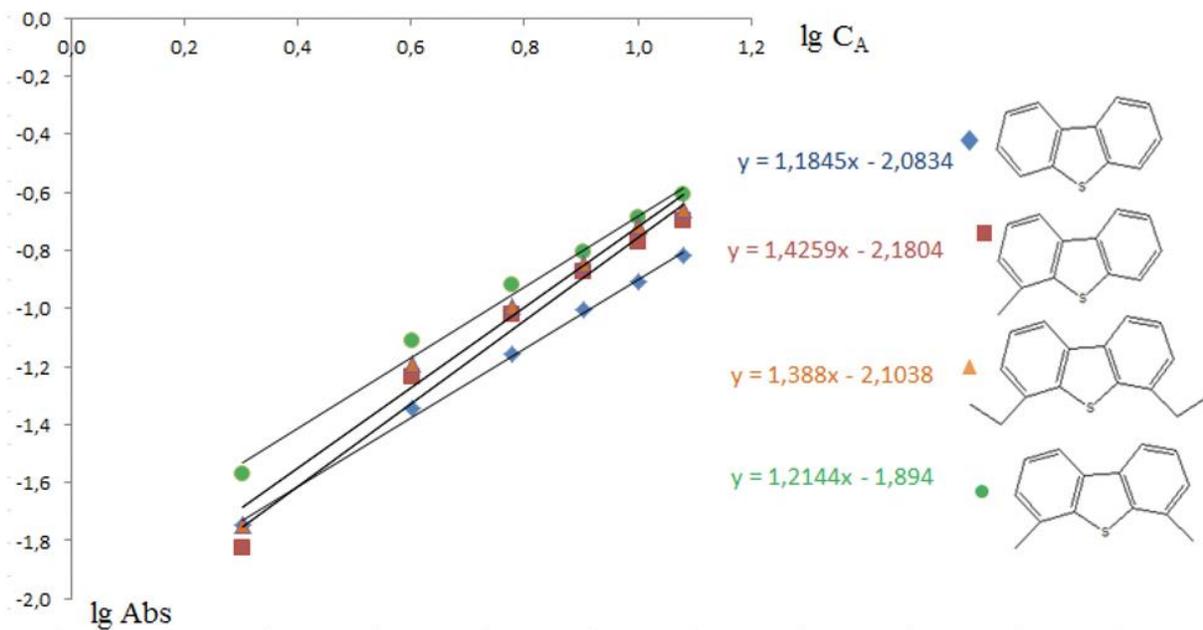| with TCNE in CHCl$_3$ | $\lambda_{max}$ in *n*-heptane, nm | $\lambda_{max}$ in isooctane, nm |
|---|---|---|
| **Dibenzothiophene** | $550 \pm 10$ | $550 \pm 10$ |
| **4MDBT** | $560 \pm 10$ | $565 \pm 10$ |
| **46DMDBT** | $560 \pm 10$ | $570 \pm 10$ |
| **46DEDBT** | $570 \pm 10$ | $580 \pm 10$ |

**Figure S1** Bilogarithmic dependence of absorbance versus the π-acceptor concentration for CTCs: DBT:TCNE, 4MDBT:TCNE, 46DMDBT:TCNE, 46DEDBT:TCNE in isooctane.
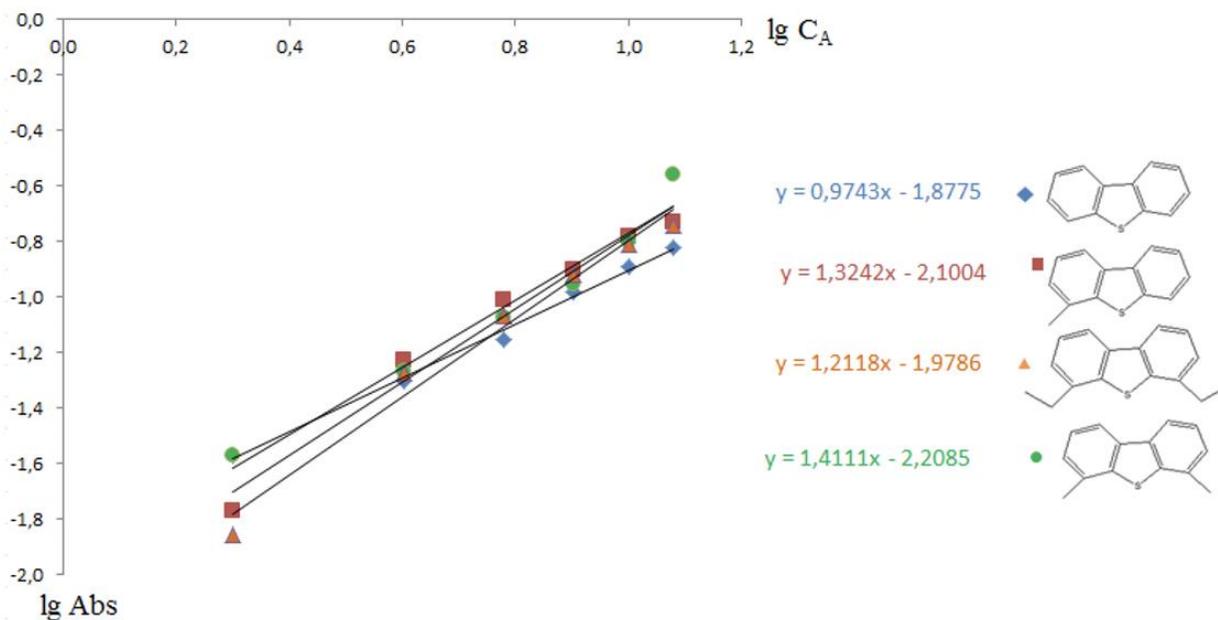


**Figure S2** Bilogarithmic dependence of absorbance versus the π-acceptor concentration for CTCs: DBT:TCNE, 4MDBT:TCNE, 46DMDBT:TCNE, 46DEDBT:TCNE in *n*-heptane.

The stoichiometric coefficients of the components of the complex correspond to the tangent of the slope of the curve ($tg\alpha$). The calculated stoichiometric ratios acceptor:donor are presented in Table S3.

**Table S3** Calculation of stoichiometric of DBTs:TCNE charge transfer complexes in isooctane by Bent-French method

| with TCNE | Equation | $tg\alpha$ |
|---|---|---|
| **Dibenzothiophene** | $\lg Abs = 1.18 \cdot \lg c_A - 1.88$ | $1.18 \pm 0.03$ |
| **4MDBT** | $\lg Abs = 1.43 \cdot \lg c_A - 2.18$ | $1.4 \pm 0.1$ |
| **46DMDBT** | $\lg Abs = 1.21 \cdot \lg c_A - 1.89$ | $1.21 \pm 0.06$ |
| **46DEDBT** | $\lg Abs = 1.39 \cdot \lg c_A - 2.10$ | $1.39 \pm 0.09$ |

**Table S4** Calculation of stoichiometric of DBTs:TCNE charge transfer complexes in *n*-heptane by Bent-French method

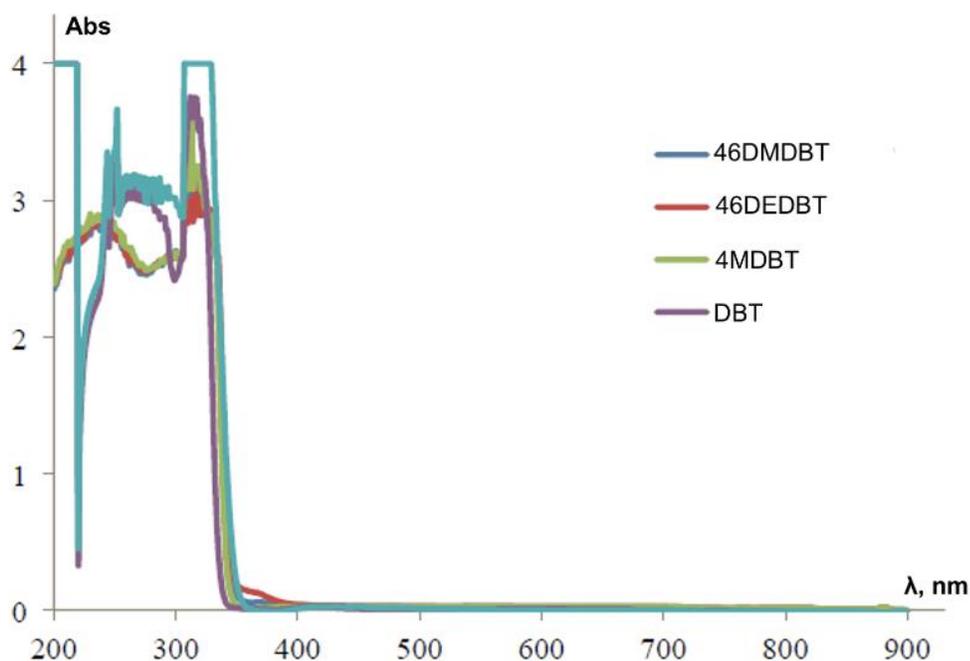| with TCNE | Equation | $tg\alpha$ |
|---|---|---|
| **Dibenzothiophene** | $\lg Abs = 0.97 \cdot \lg c_A - 1.88$ | $0.97 \pm 0.03$ |
| **4MDBT** | $\lg Abs = 1.32 \cdot \lg c_A - 2.10$ | $1.3 \pm 0.1$ |
| **46DMDBT** | $\lg Abs = 1.41 \cdot \lg c_A - 2.21$ | $1.4 \pm 0.1$ |
| **46DEDBT** | $\lg Abs = 1.21 \cdot \lg c_A - 1.98$ | $1.2 \pm 0.1$ |



**Figure S3** UV-vis spectra of individual solutions of DBT and its derivatives (10 mM) in chloroform.
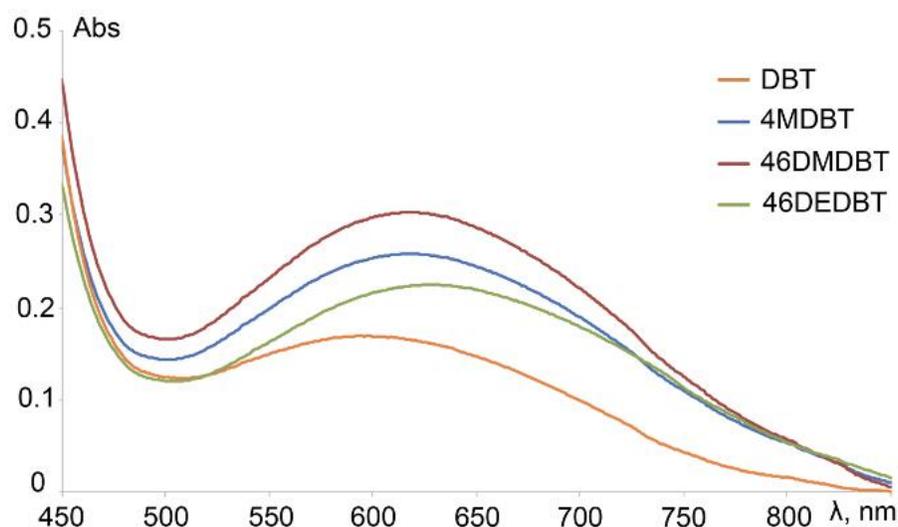
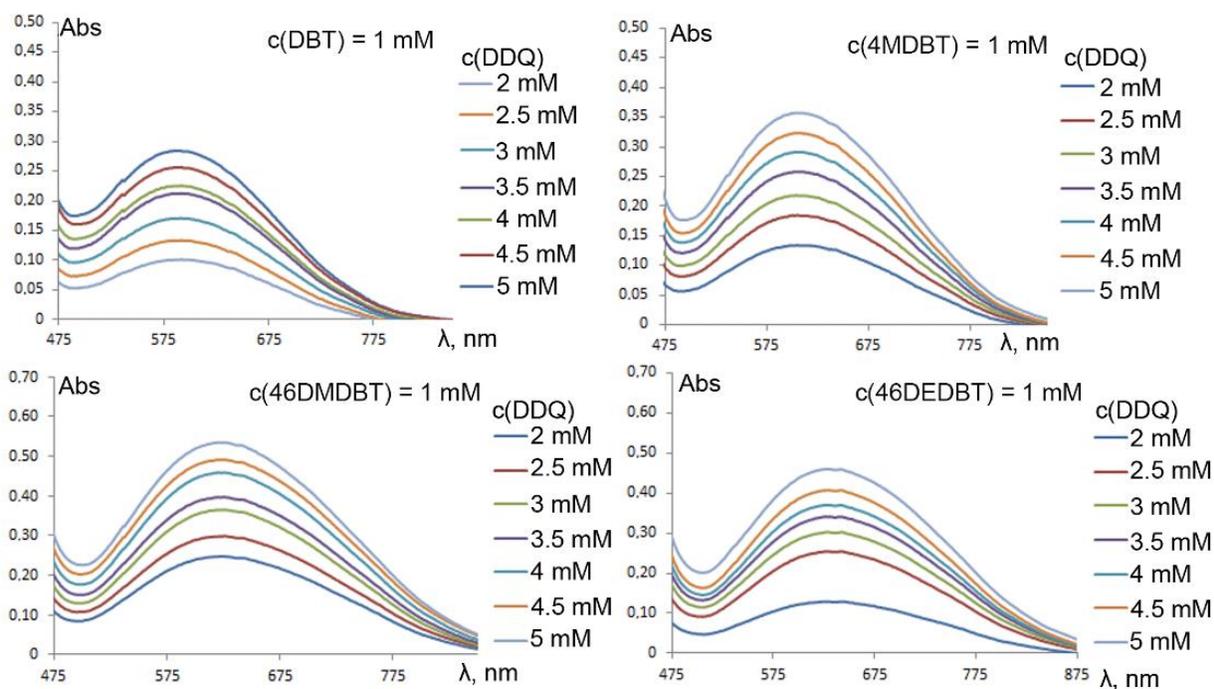**Figure S4** UV-vis spectra of DBT, 4MDBT, 46DMDBT, and 46DEDBT (1 mM) in isooctane with DDQ (5 mM) in CHCl$_3$.



**Figure S5** UV-vis spectra of DBT, 4MDBT, 46DMDBT, and 46DEDBT (1 mM) in *n*-octane with different concentrations of DDQ in CHCl$_3$.
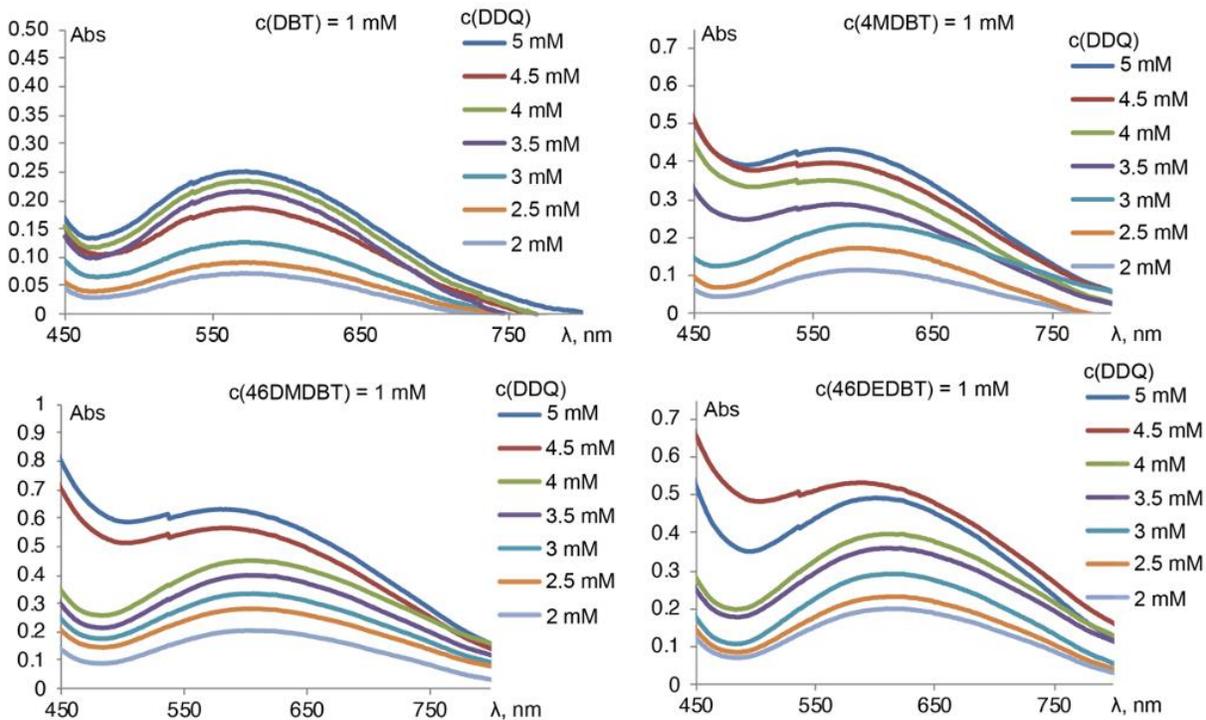
**Figure S6** UV-vis spectra of DBT, 4MDBT, 46DMDBT, and 46DEDBT (1 mM) in *n*-heptane with different concentrations of DDQ in CHCl₃.
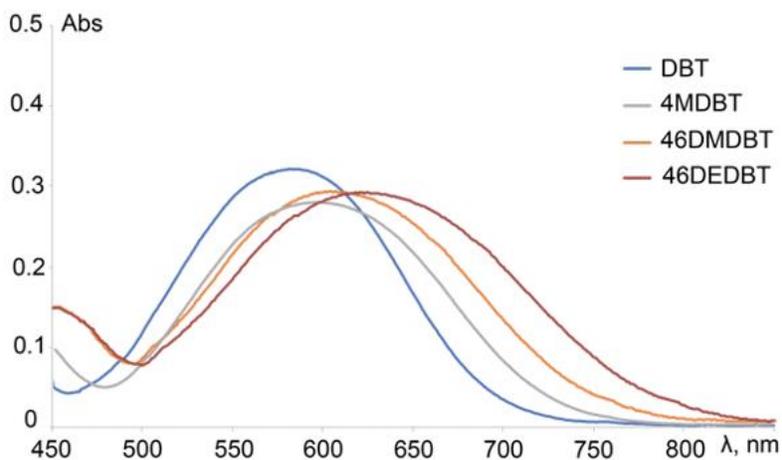


**Figure S7** UV-vis spectra of DBT, 4MDBT, 46DMDBT, and 46DEDBT (1 mM) in isooctane with TCNE (5 mM) in CHCl₃.
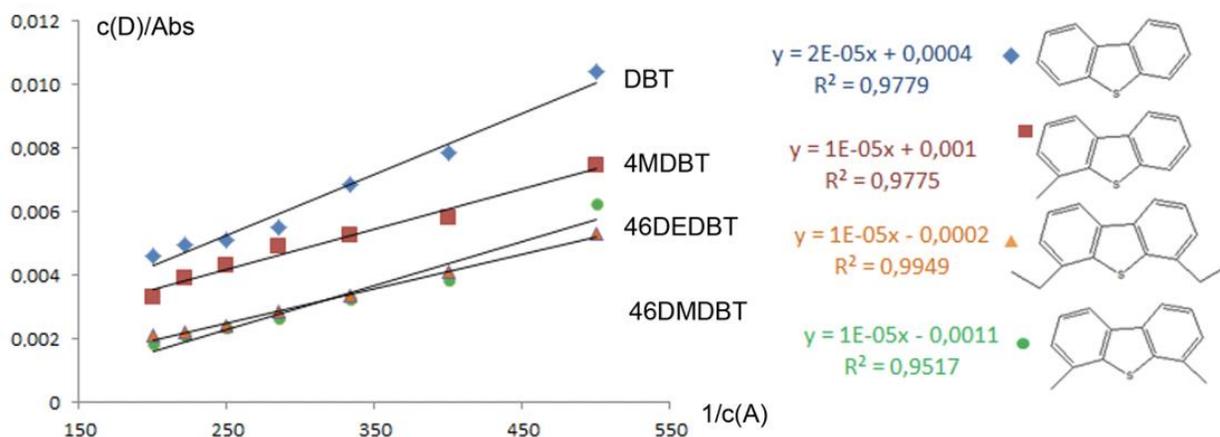
**Figure S8** Linearized curves for calculation of stability constants of DBT, 4MDBT, 46DMDBT, and 46DEDBT in *n*-heptane.
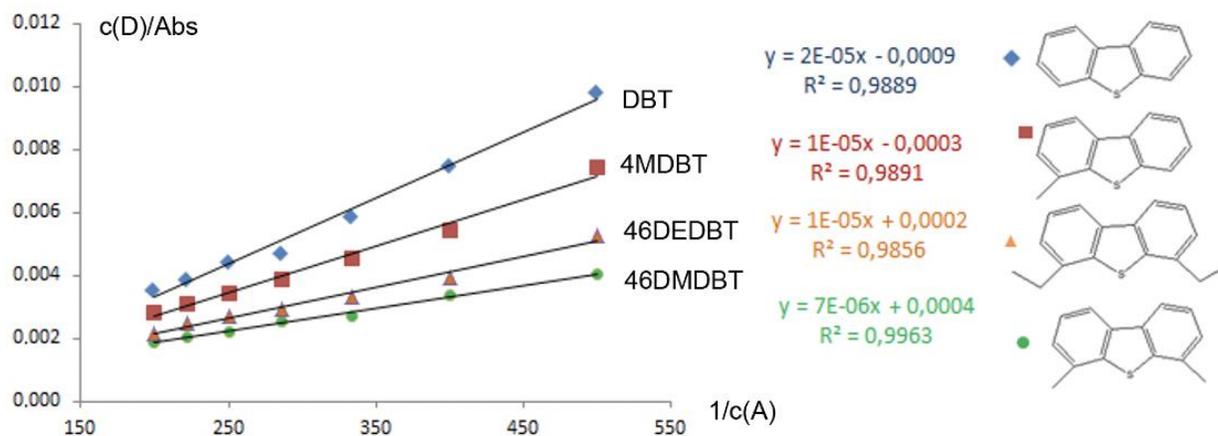


**Figure S9** Linearized curves for calculation of stability constants of DBT, 4MDBT, 46DMDBT, and 46DEDBT in *n*-octane.

**Table S5** Stability constants ($K_f$) of charge transfer complexes with DDQ in *n*-heptane, *n*-octane, and isooctane

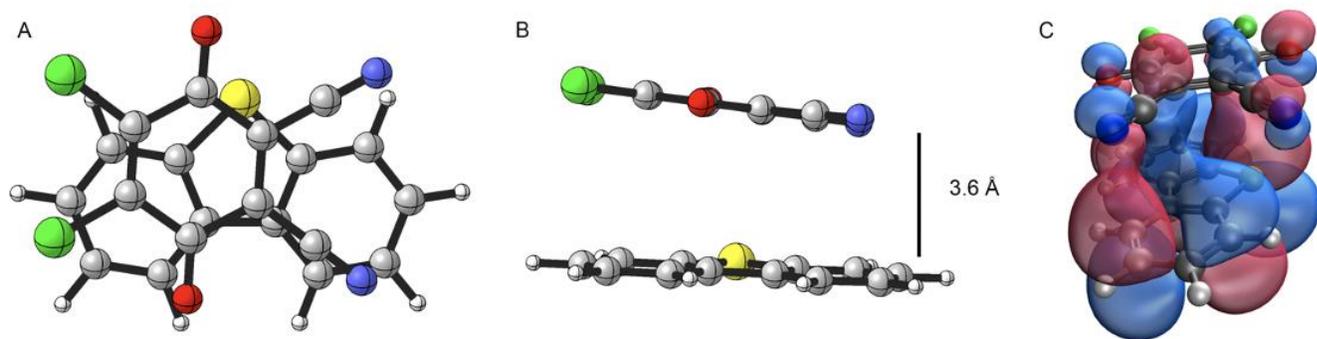| with DDQ in CHCl$_3$ | $K_f$ in *n*-heptane, L/mol | $K_f$ in *n*-octane, L/mol | $K_f$ in isooctane, L/mol |
|---|---|---|---|
| **Dibenzothiophene** | $20 \pm 1$ | $45 \pm 5$ | $20 \pm 1$ |
| **4MDBT** | $100 \pm 12$ | $30 \pm 7$ | $50.0 \pm 0.3$ |
| **46DMDBT** | $110 \pm 13$ | $58 \pm 4$ | $143 \pm 8$ |
| **46DEDBT** | $20 \pm 3$ | $20 \pm 7$ | $50.0 \pm 0.3$ |

**Figure S10** Charge transfer complex of DBT with DDQ (A and B). LUMO of the charge transfer complex formed by DBT and DDQ (C).

Three-dimensional structures and orbital plots were produced with IQMol 2.15.