Structure-Properties Relationships in Boron-Doped Polycyclic Aromatics

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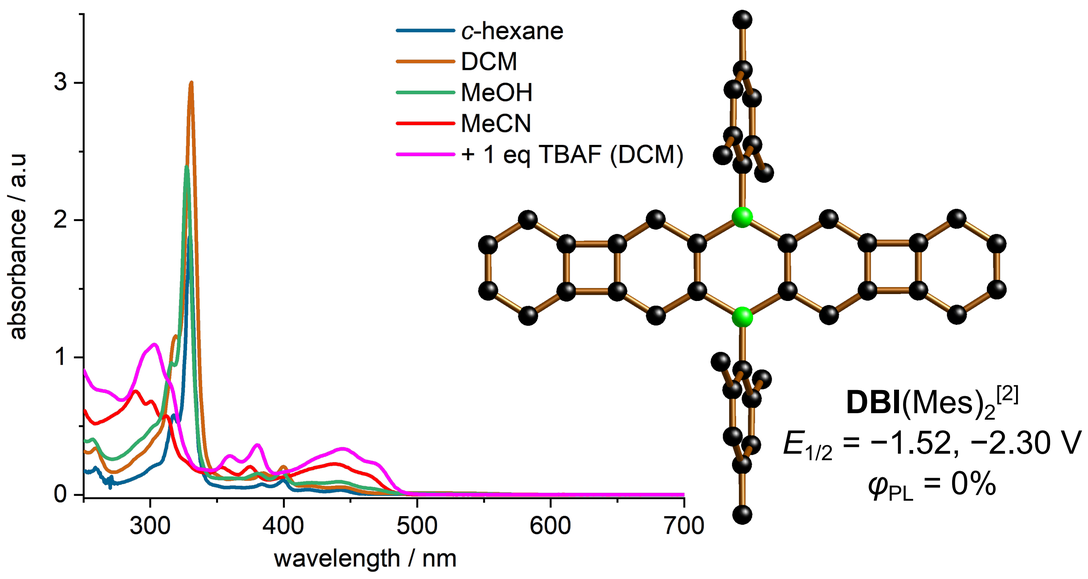
Introduction

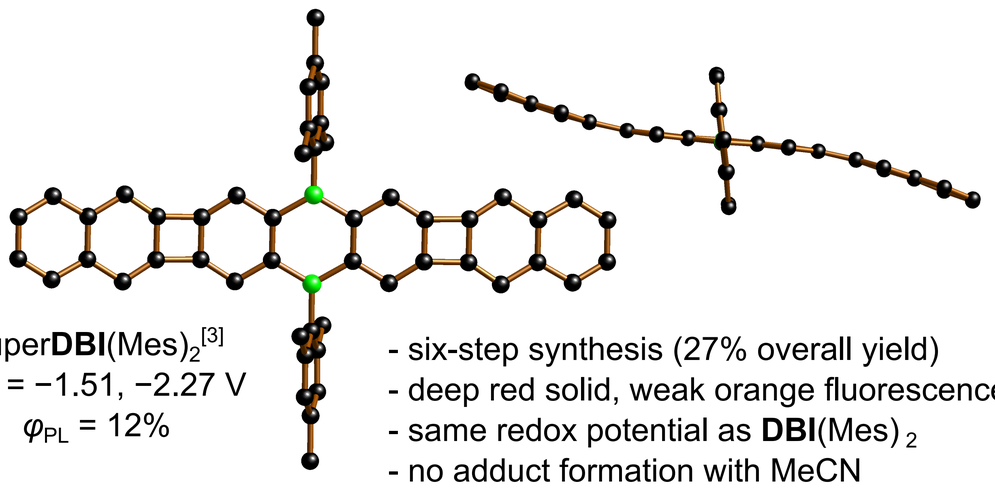
The substitutional doping of polycyclic aromatic hydrocarbons (PAHs) with main-group elements such as boron (B-PAHs) provides access to new organic materials.[1] In spite of their great application potential, e.g., in organic light-emitting devices, only little systematic research has been performed regarding the effect of π-extension on the electronic structures of B-PAHs. We therefore synthesised a series of closely related molecules and investigated their optoelectronic properties by experimental[a] and theoretical[b] means.

Phenylene-Containing Oligoacenes



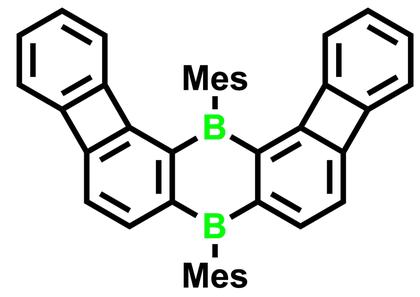
DBI(Mes)$_2$[2]
$E_{1/2}$ = −1.52, −2.30 V
φ_{PL} = 0%

- five-step synthesis (31% overall yield)
- deep red solid, non-fluorescent
- lack of fluorescence due to optically forbidden S_1
- non-radiative deactivation via a low-lying doubly excited state
- comparatively high electron affinity without EWG attached
- potent yet water-stable Lewis acid: quant. adducts with MeCN and F^-

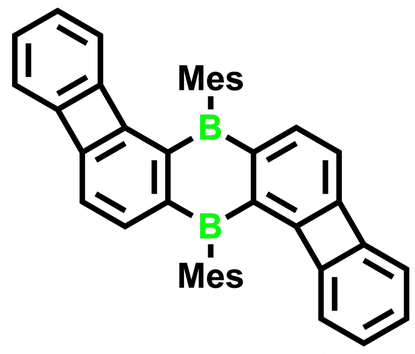


superDBI(Mes)$_2$[3]
$E_{1/2}$ = −1.51, −2.27 V
φ_{PL} = 12%

- six-step synthesis (27% overall yield)
- deep red solid, weak orange fluorescence
- same redox potential as **DBI**(Mes)$_2$
- no adduct formation with MeCN
- sigmoidal curvature in the solid state

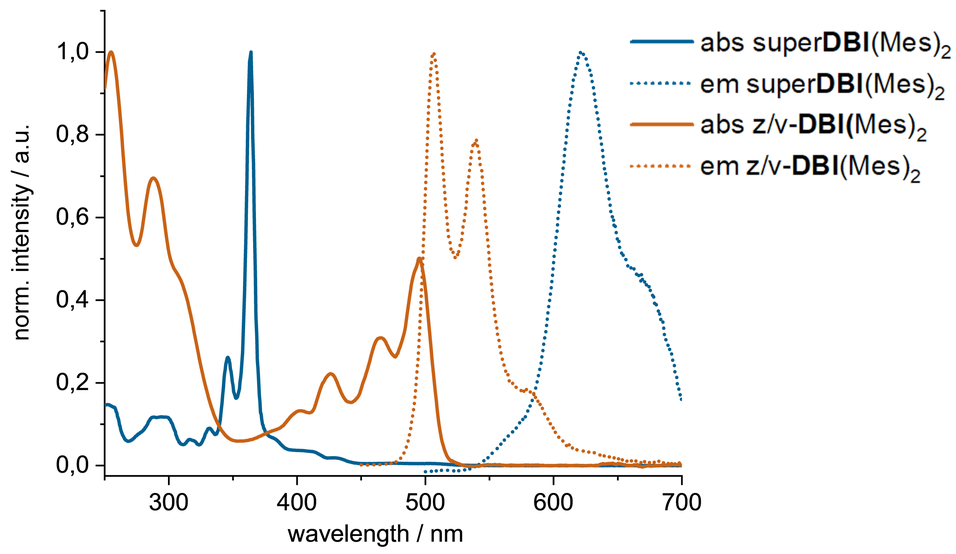


v-**DBI**(Mes)$_2$[3]
$E_{1/2}$ = −1.82, −2.51 V
φ_{PL} = 65%
values given for the 12:1 v:z-mixture

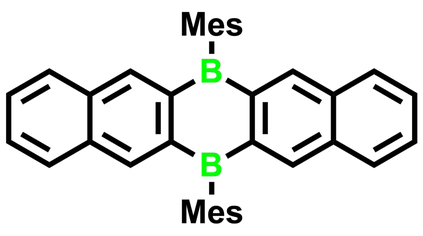


z-**DBI**(Mes)$_2$[3]

- five-step synthesis (5% overall yield)
- non-selective synthesis of z/v-isomeric mixture
- orange solid, strong green fluorescence
- lower electron affinity compared to the other **DBI**-derivatives
- no adduct formation with MeCN

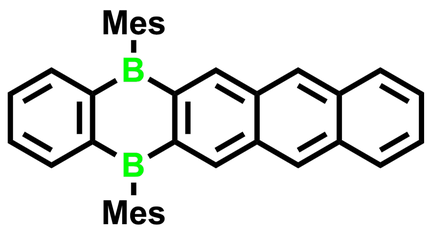


Regular Oligoacenes



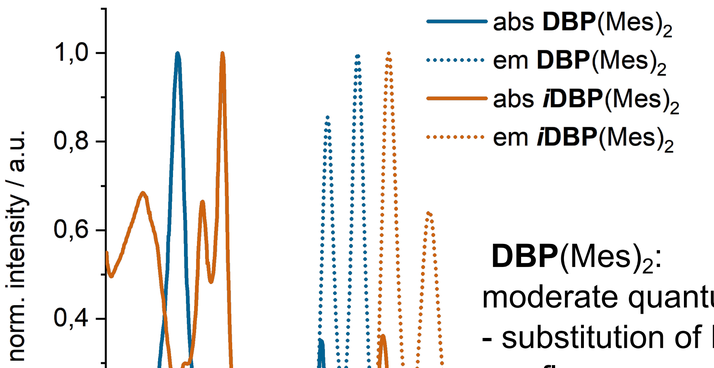
DBP(Mes)$_2$[2]
$E_{1/2}$ = −2.03, −2.75 V
φ_{PL} = 47%

- five-step synthesis (18% overall yield)
- low electron affinity
- no adduct formation with MeCN



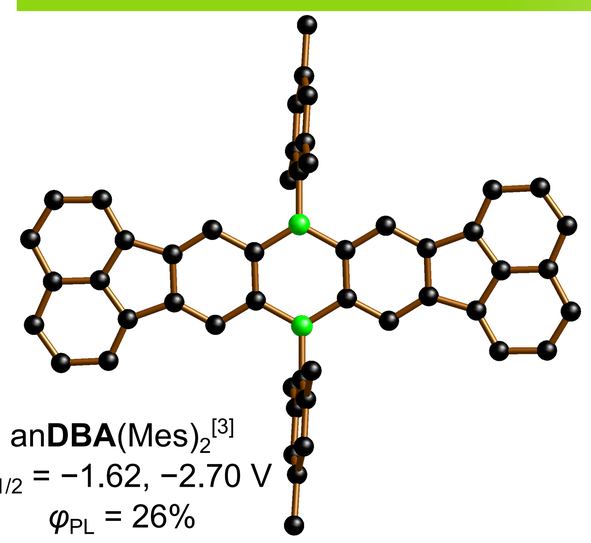
*i***DBP**(Mes)$_2$[2]
$E_{1/2}$ = −1.99 V
φ_{PL} = 87%

- three-step synthesis (38% overall yield)[4]



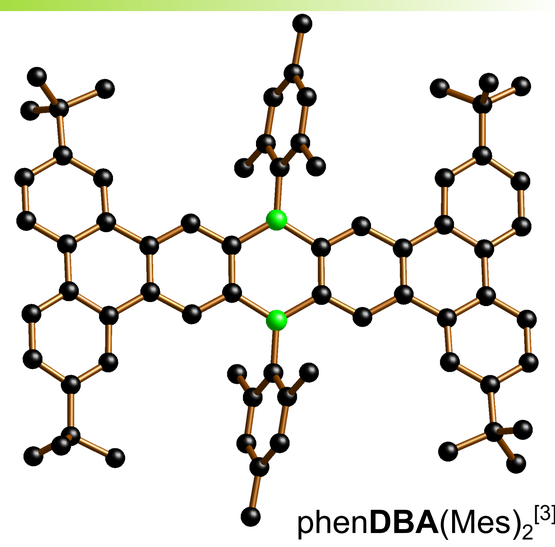
DBP(Mes)$_2$:
moderate quantum yield: charge transfer Mes→B
- substitution of H or F instead of *p*-CH_3
→fluorescence boost (up to 90%)

Polycyclic Hydrocarbons



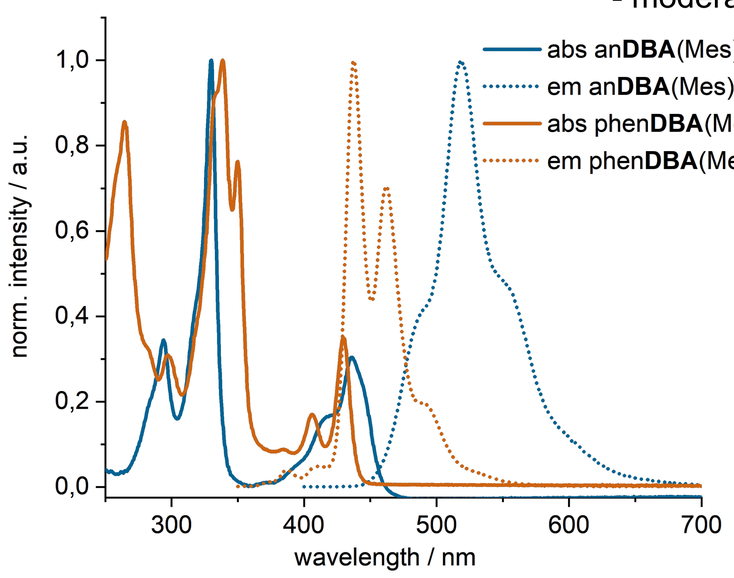
anDBA(Mes)$_2$[3]
$E_{1/2}$ = −1.62, −2.70 V
φ_{PL} = 26%

- five-step synthesis (23% overall yield)
- electron affinity close to that of the **DBI**-derivatives
- partial adduct formation with MeCN
- rather weak green fluorescence, larger Stokes-shift compared to the other derivatives



phenDBA(Mes)$_2$[3]
$E_{1/2}$ = −1.82, −2.44 V
φ_{PL} = 56%

- six-step synthesis (4% overall yield)
- lowest electron affinity of the series
- no adduct formation with MeCN
- moderate blue fluorescence



[1]: Review articles: E. Grotthuss, A. John, T. Kaese, M. Wagner, *Asian J. Org. Chem.* **2018**, *7*, 37-53; A. Escande, M. J. Ingleson, *Chem Commun* **2015**, *51* , 6257-6274.
[2]: S. Kirschner, J.-M. Mewes, M. Wagner *et al.*, *Chem. Eur. J.* **2017**, 23, 5104-5116.
[3]: S. Kirschner, J.-M. Mewes, M. Wagner, *manuscript in preparation*.
[4]: A. John, M. Wagner *et al.*, *Angew. Chem. Int. Ed.* **2017**, 56, 5588-5592

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