Supporting Information:

Mixed-Valence Cations of Di(carbazol-9-yl) Biphenyl, Tetrahydropyrene, and Pyrene Derivatives

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Vis-NIR spectra obtained stepwise oxidation of **1b**	pS2
TD-DFT-calculated spectra for **Ib**$^{\bullet+}$ and **II**$^{\bullet+}$-**IV**$^{\bullet+}$	pS3
Orbitals involved in TD-DFT-calculated transitions for **4b**$^{\bullet+}$	pS4
Partial MO diagram for **Ib**, **II**$^{\bullet}$ and **III**	pS5
Reorganization energies for self-exchange reactions	pS6
Complete citations for references 30, 32, 57, 59, 62, and 70	pS7
References for Supporting Information	pS8

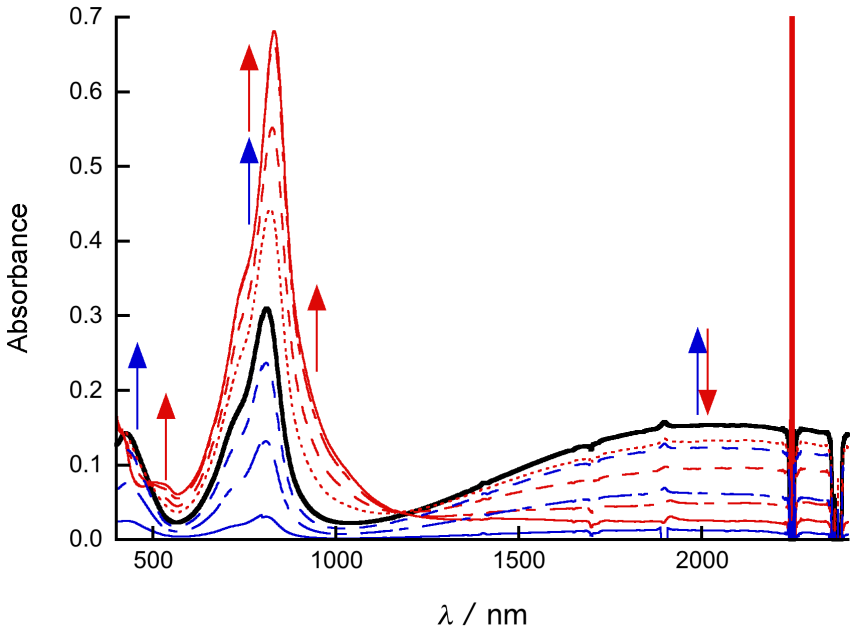

Figure S1. Selected Vis-NIR spectra obtained during the stepwise oxidation of **1b** with $SbCl_5$ in CH_2Cl_2. Spectra shown in blue were acquired on partial oxidation from the neutral compound to the monocation (spectra shown with solid, dot-dash, and dash lines corresponding to increasing quantities of oxidant). The spectrum shown in black was acquired on complete oxidation to the monocation (identified as such by the absorptivity of the long-wavelength NIR band being at a maximum). Spectra in red were acquired on oxidation from the monocation to the dication (dot, dash, dot-dash, and solid lines corresponding to successively greater quantities of oxidant). Blue and red arrows highlight the changes in band strength on conversion to mono- and dications respectively.

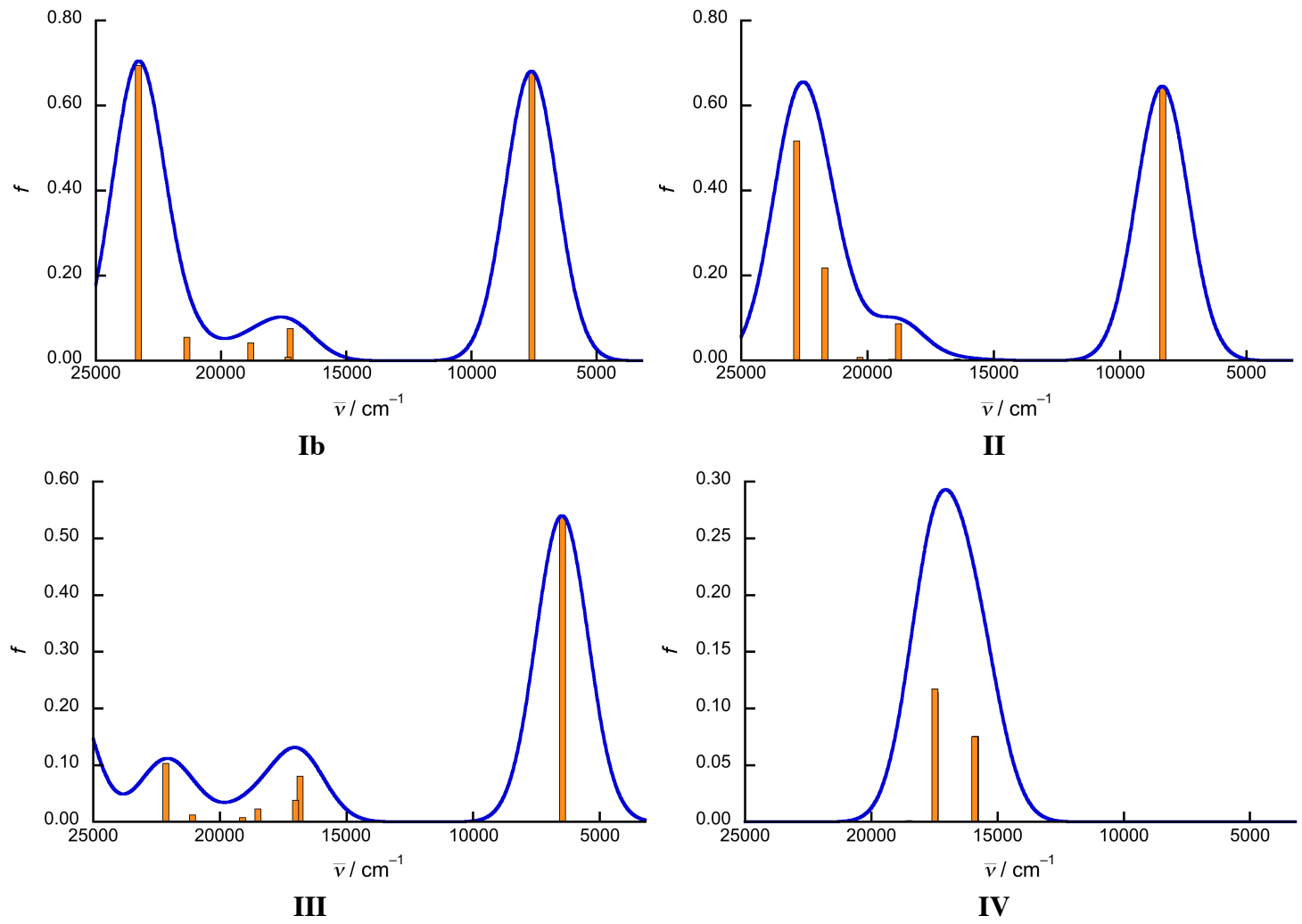

Figure S2. TD-DFT-calculated spectra of the monocations of bis(di-*p*-tolylamino) derivatives of biphenyl, tetrahydropyrene, and pyrene and of the tri-*p*-tolylamine radical cation (transition energies and oscillator strengths indicated by orange bars; spectra, in blue, obtained by applying a Gaussian broadening). Note that the vertical scale varies between the spectra. Note also that the TD-DFT spectra for **1b**$^{\bullet+}$**-3b**$^{\bullet+}$ are based on delocalized radical-ion structures. Note that an experimental spectrum of **Ib**$^{\bullet+}$ is shown in ref. S1.

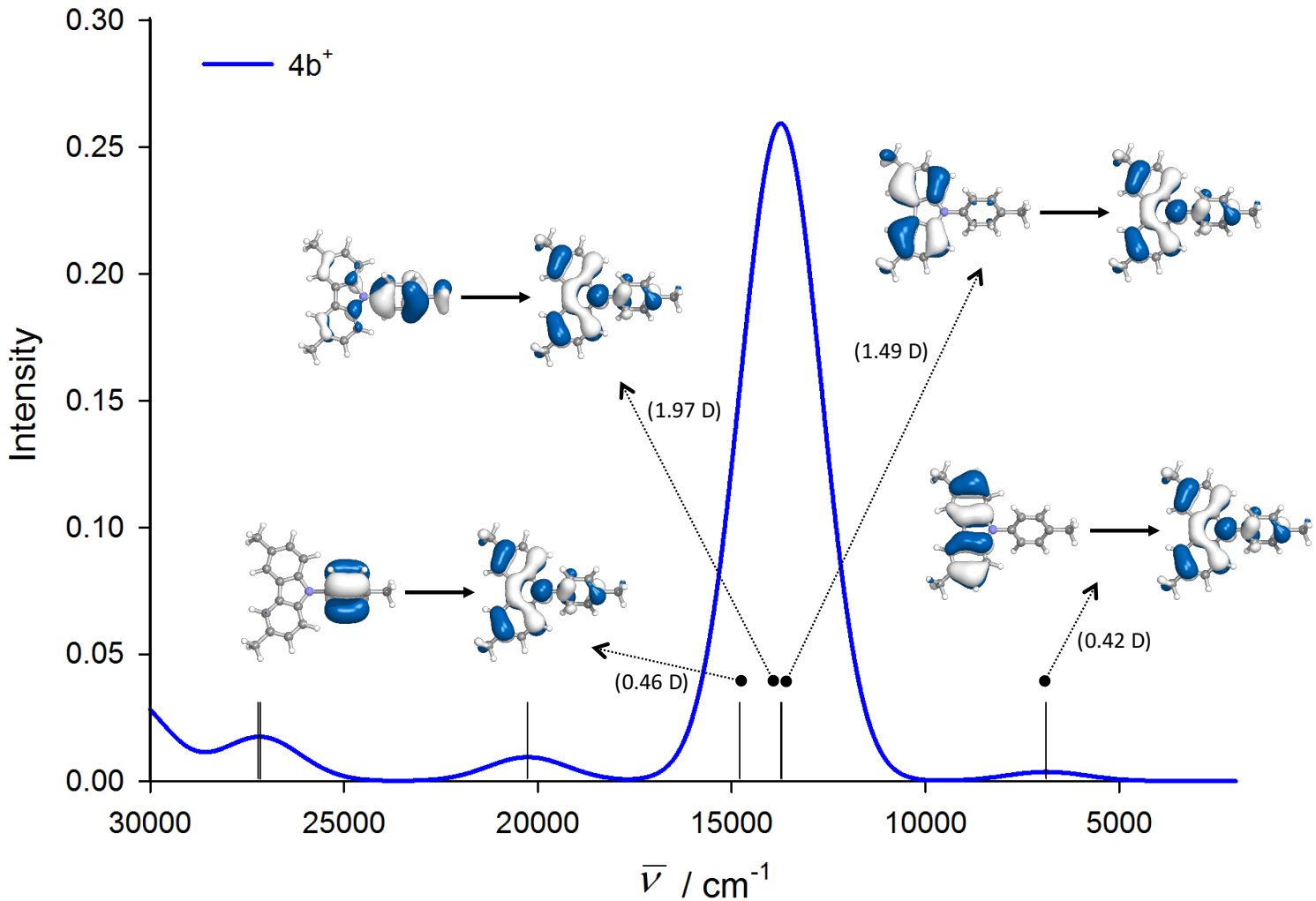

Figure S3. TD-DFT-calculated spectrum for **4b**$^{\bullet+}$ showing the main orbitals involved in the three transitions that contribute to the strong visible absorption, and those involved in the weak near-IR transition.

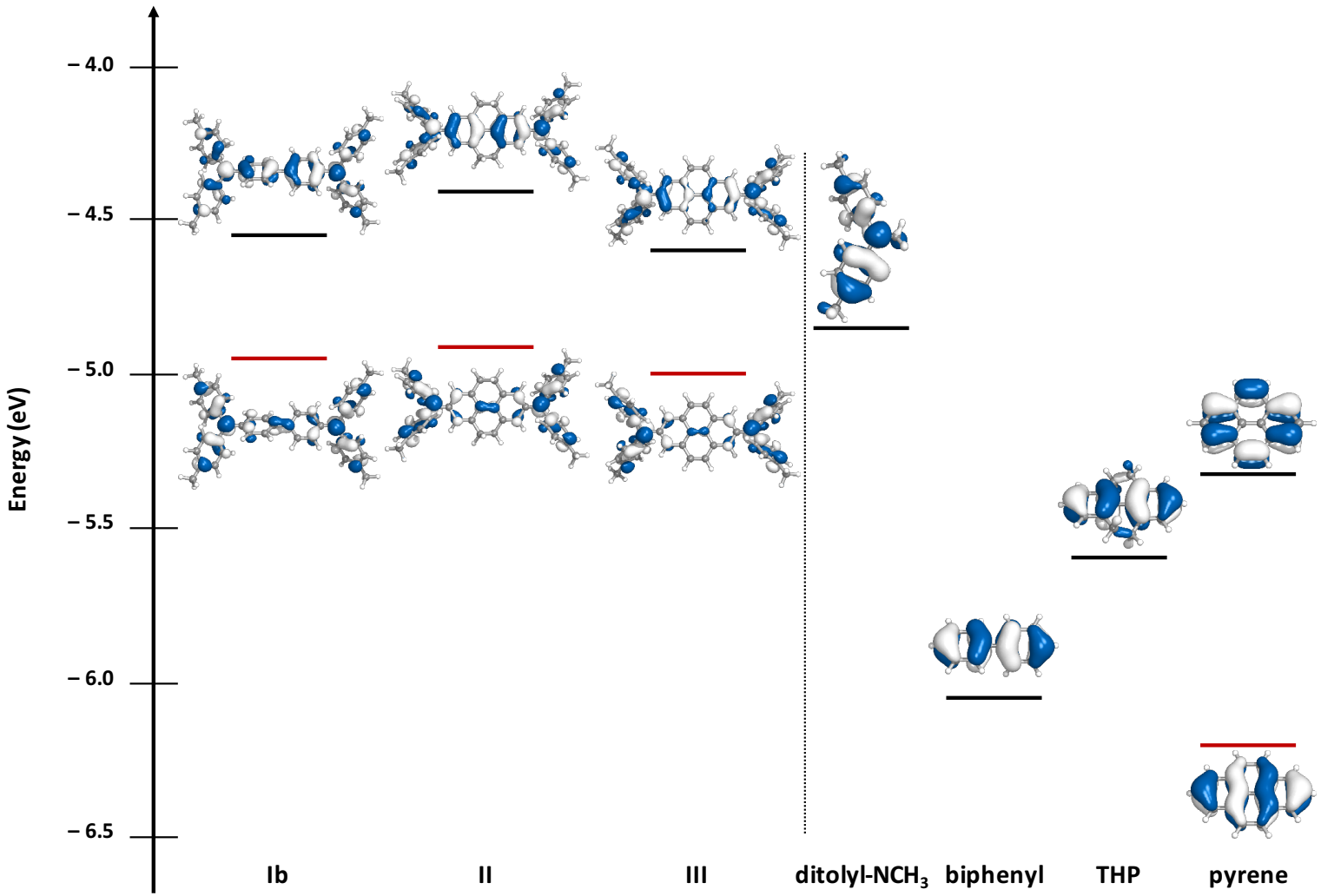

Figure S4. Selected orbitalsB3LYP/6-31G(d,p)-calculated molecular orbitals for **Ib**, **II**, and **III** (with ^{t}Bu groups replaced by Me) and for end-group (modeled as *N*-methyl-di-*p*-tolylamine) and bridge (biphenyl, 4,5,9,10-tetrahydropyrene (THP), and pyrene) fragments. Black and red denote HOMO and HOMO–1 respectively.

Table S1. DFT-Calculated Reorganization Energies (meV) for Self-Exchange Reactions[a]

Compound	$\lambda_{(neut)}$	$\lambda_{(cat)}$	λ_i
1b/1b$^{\bullet+}$	58.8	53.2	112.0
2b/2b$^{\bullet+}$	77.8	72.9	150.7
3b/3b$^{\bullet+}$	45.6	43.8	89.4
4b/4b$^{\bullet+}$	70.4	66.3	136.7
Ib/Ib$^{\bullet+}$	122.2	105.7	228.3
IIb/IIb$^{\bullet+}$	54.2	127.0	265.1
IIIb/IIIb$^{\bullet+}$	70.4	68.7	139.1
IVb/IVb$^{\bullet+}$	61.1	64.9	126.0

[a] Total intramolecular reorganization energy $\lambda_i = \lambda_{(neut)} + \lambda_{(cat)}$, where $\lambda_{(neut)}$ and $\lambda_{(cat)}$ are the relaxation energies of neutral species and cationic species, respectively, following electron transfer.

Complete Citations for References 30, 32, 57, 59, 62, and 70

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