

Supplementary Information

Electronic Properties of Viologen–Tetraarylborate Complexes: Dynamics of Radical Pairs and Optical Switching Effects Modulated by Microwave Radiation

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Materials and Methods

Materials

3,3,5,5-Tetramethyl-1-pyrroline N-oxide (TMPO), potassium tetraphenylborate, potassium tetra(p-toluy)borate, potassium tetra(p-biphenyl)borate, potassium tetra(4-Chlorophenyl)borate, methylviologen dichloride ($MV^{2+}2Cl^-$), benzylviologen dichloride ($BzV^{2+}2Cl^-$), and all solvents: tetrahydrofuran (THF) and acetonitrile (ACN), methanol (MetOH) - HPLC grade, were purchased from Sigma-Aldrich and used without further purification.

Ion-pair complexes (viologen-tetraarylborate) were obtained by mixing viologen dichloride (1×10^{-3} mol L⁻¹) and potassium tetraarylborate (2×10^{-3} mol L⁻¹) in a 1:1 methanol/H₂O solution. After stirring for 2 hours at 298 K, a colored compound precipitates from the solution. The solution was filtered, the solid was washed with methanol (150 mL) and dried in desiccator at low pressure. Following recrystallization, the resulting complex was used in all experiments.

Thin films of the copolymer poly(ethylene vinyl acetate - PEVA) were prepared with ion-pair complexes incorporated in the polymer matrix. The sequence of film preparation was as follows: 3.30 mg of the ion-pair complex was dissolved in THF and a 60 mg amount of the polymer was added to the same solution. After mixing, the resulting solution was transferred to a Teflon plate and kept at room temperature for 24 hours. After this time period, the polymer solution was dried at 313 K for 12 hours and dried again at 313 K for 12 hours at low pressure.

Spectroscopic Measurements

UV-vis absorption and fluorescence. Absorption spectra were recorded using a Multiskan Go Reader (Thermo Scientific, Waltham MA, US) spectrophotometer and a Shimadzu UV 3600 spectrophotometer coupled to a diffuse reflectance accessory

(Hitachi-Hitech, Tokyo, Japan). Fluorescence and excitation spectra were recorded with a Hitachi F4500 (Hitachi-Hitech, Tokyo, Japan) spectrofluorimeter.

Time-resolved fluorescence. Fluorescence decays were measured using the time-correlated single-photon counting technique. Laser pulses at 400 nm were provided by frequency doubling a laser pulse of 150 fs temporal duration (Ti-Sapphire Mira 900 laser pumped by Verdi 5 W, Coherent). The fluorescence decays were collected under magic angle (54.7°) polarization conditions. The instrument response function (irf) was 40 ps (FWHM). All complex solutions had an optical density of about 0.2 at 410 nm. The decay time profiles were recorded with a TC900 counting board and software from Edinburgh Instruments. Lifetimes were evaluated using the Deconvolution procedure with a three-exponential decay model, according to eq 9.

$$I(t) = \sum_1^3 B_i \exp(-t/\tau_i) \quad (9)$$

Here, τ_i and B_i are the respective decay time constant and the pre-exponential factor for each component (i).

Laser Flash Photolysis. Triplet–singlet difference absorption spectra were obtained using an Applied Photophysics laser flash photolysis apparatus pumped by the third harmonic (355 nm) of a Nd:YAG laser (Spectra Physics) with an excitation wavelength of 266 nm and a 4 ns pulse duration, monitoring the optical density change at 10 nm wavelength intervals. Prior to the measurement, anaerobic conditions were achieved by purging the samples for 30 min with high-purity argon (White-Martins, Sertãozinho-SP, Brazil).

Steady State Electron Paramagnetic Resonance (SSEPR) spectroscopy. X-band (9.5 GHz) EPR measurements were carried out using a Bruker EMX plus spectrometer at 298 K in a Suprasil quartz tube with 100 kHz magnetic field modulation of 0.1 or 1.0 G amplitudes. In a typical experiment, a solution of 100 μ L of the complex (1×10^{-4} M) was prepared in an oxygen-free environment. Irradiation of the solution (or solid) samples was carried out with a continuous laser source at 410 ± 10 nm.

Femtosecond Transient Absorption. The set-up used for transient absorption measurements is based on a regeneratively amplified Ti:Sapphire laser system (Spitfire Pro, Spectra-Physics, 1kHz) that generates 35 fs (fwhm) 3.8 mJ pulses centered at 800 nm. The output is split 50:50 into two beams. The first beam sent to a TOPAS-C optical parametric amplifier to produces 480, and 350 nm pulses, which were used for sample excitation. The second beam was attenuated, sent through a computer-controlled optical stage to adjust the time delay with respect to the excitation pulse, and then focused onto a 2 mm CaF₂ window to produce a white-light continuum (wlc) probe spanning the 345-690 nm range. The wlc probe beam was focused to a 75 μm diameter spot at the sample and overlapped nearly collinearly (angle, 1°) with the excitation beam focused to a 150 μm diameter spot. A fraction of the wlc probe beam was split off before the sample to be utilized as a reference for the correction of the shot-to-shot pulse-intensity fluctuations. The probe (after the sample) and reference beams were dispersed by a spectrograph and recorded using a dual CCD detector synchronized to the 1 kHz repetition rate. The difference between the decadic logarithms of a probe-to-reference intensity ratio measured at a specific position of the optical stage for excitation on and off represents the change in the sample absorbance (ΔA) at the corresponding delay time. The solutions were circulated through a flow cell with a 2-mm path length. The zero time delay is obtained from the non-resonant electronic response from neat solvents measured at the same experimental conditions. The typical excitation energy was 3.1 μJ·pulse⁻¹ and the linearity of ΔA signals with excitation energy confirmed that single-photon excitation is responsible for the measured data. The polarization of the excitation beam was set at the magic angle (54.7°) with respect to the probe beam to eliminate solute rotational signals. All experiments were performed at 21 °C.

II.3 DFT Calculations

Time Dependent - Density functional theory (DFT) calculations were performed with the Gaussian 09 (G09) program package, employing the functional B3LYP. The basis set 6-31+(d) was used to optimize the gas phase singlet or doublet geometries.

Table Section

Table S1. Decay lifetime (τ_i) and percentage amplitude (B_i %) of ion-pair complexes studied in this work obtained by using a three-exponential decay fitting model.

System	E_{00} (eV)	Component (i)	aB_i %	τ_i (ns)
1a:2a	-	1	49.4 ^[b]	0.47b
		2	40.0 ^[b]	2.28b
		3	10.4 ^[b]	7.91b
1b:2a	2.42	1	84.7 ^[b]	0.20b
		2	11.8 ^[b]	2.20b
		3	3.48 ^[b]	7.50b
1b:2b	2.40	1	43.8	0.08
		2	39.3	0.92
		3	16.9	3.93
1b:2c	2.41	1	27.1	0.10
		2	48.2	0.84
		3	24.7	3.04

^aB is the pre-exponential factor in the model function for exponential component analysis, $B_i\% = 100 \times (B_i/\sum B_i)$. ^bvalues from literature.¹⁴

Table S2. Hyperfine coupling constants used for simulations.

Complex	a_N (#nuclei)	$a_{H\alpha}$ (#nuclei)	$a_{H\beta}$ (#nuclei)	$a_{H\gamma}$ (#nuclei)
1a:2a	4.70 (2)	4.60 (4)	1.40 (4)	1.42 (6)
1b:2a	4.00 (2)	2.70 (4)	2.70 (4)	1.30 (4)
1b:2b	4.24 (2)	2.57 (4)	1.50 (4)	1.50 (4)
1b:2c	4.60 (2)	3.20 (4)	1.40 (4)	1.60 (4)

Figure Section

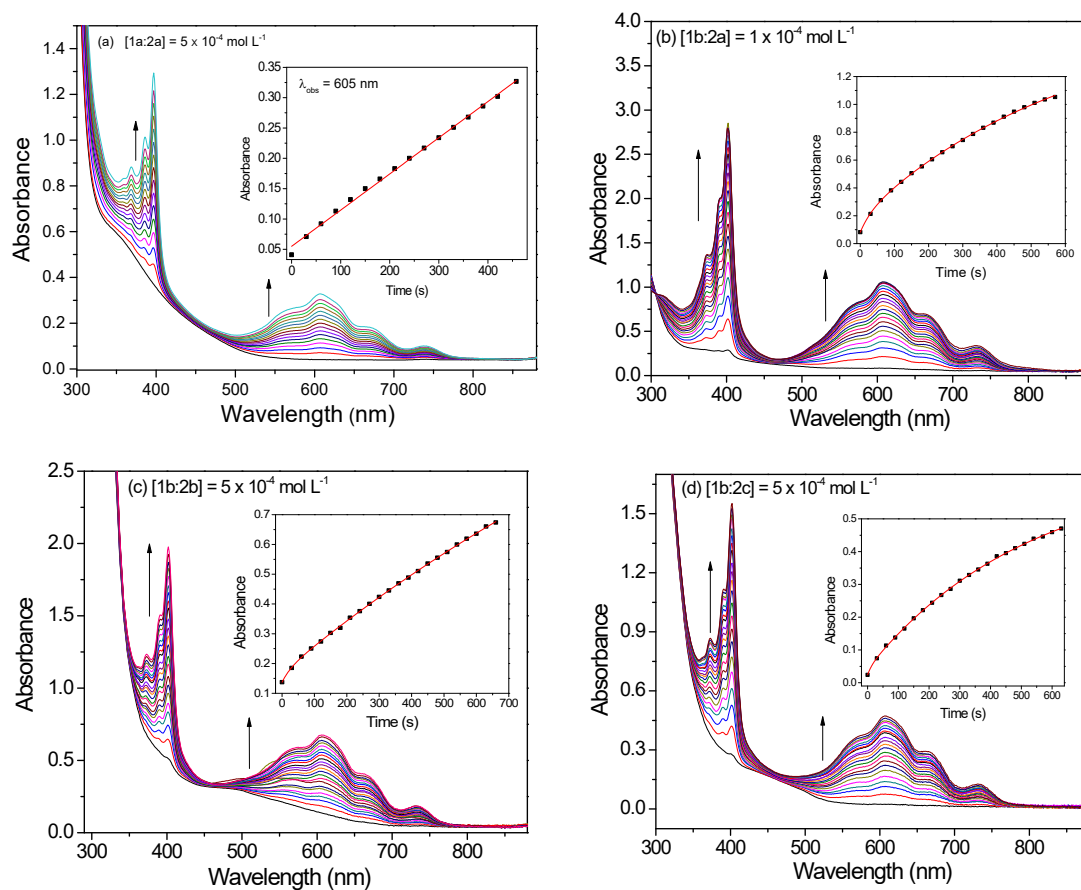


Figure S1. UV-vis absorption spectra of the viologen:borate complex at different times of irradiation in THF:ACN (5:1 v/v) solvent. Complex system: (a) 1a:2a, (b) 1b:2a, (c) 1b:2b and (d) 1b:2c.

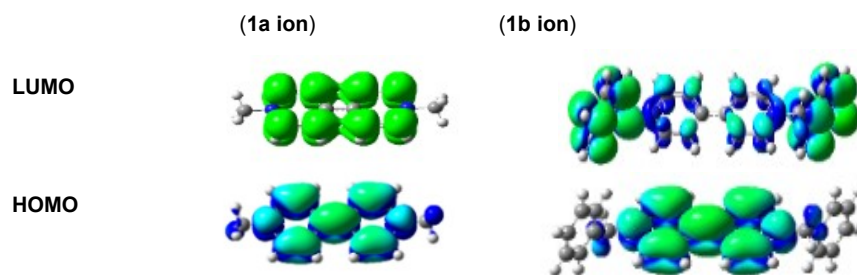


Figure S2. Molecular electrostatic potential surface (MESP) for **1a** and **1b** viologen structures in the HOMO and LUMO levels.

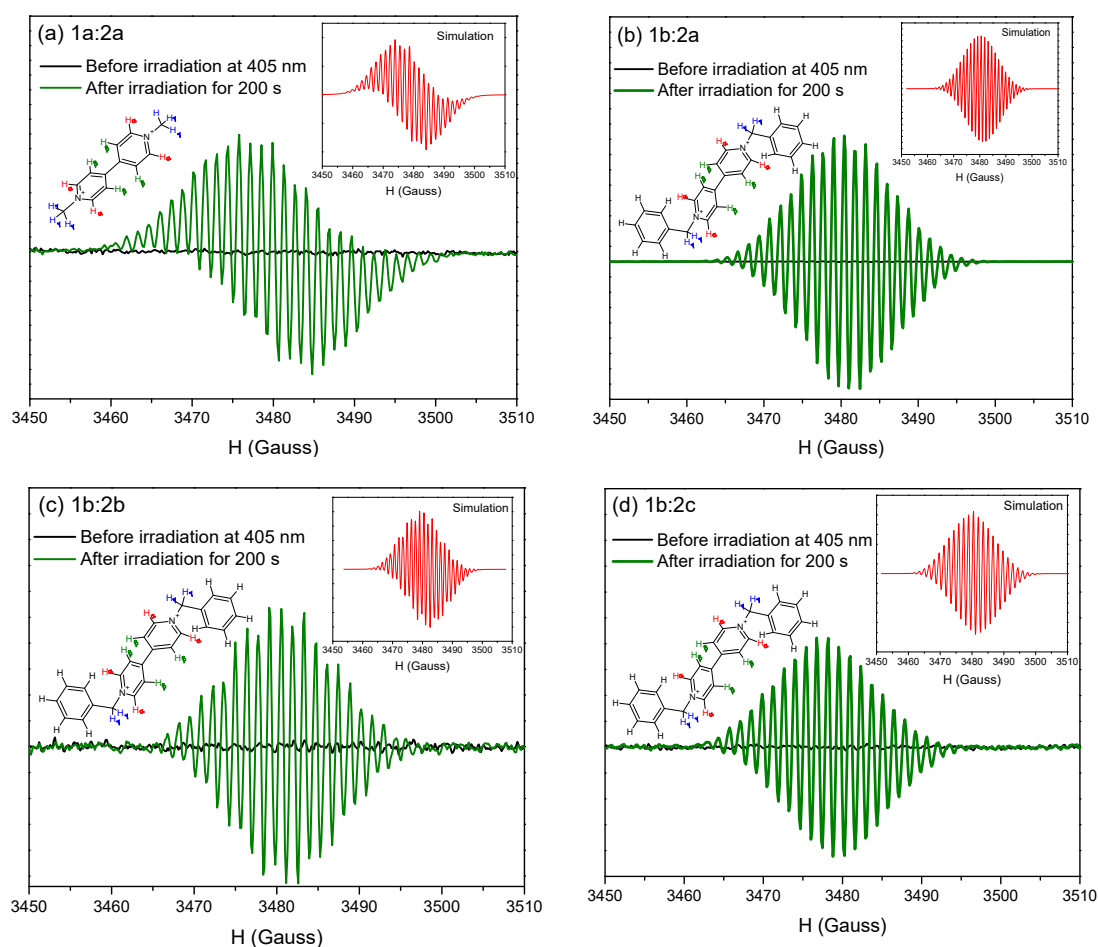


Figure S3. EPR signal of the viologen:borate complex in THF:ACN (5:1 v/v) after 2 min of irradiation at 410 nm. Complex system: (a) 1a:2a, (b) 1b:2a, (c) 1b:2b and (d) 1b:2c.

DFT Calculations

Methylviologen dication (1a ion)

Charge = 1 Multiplicity = 2

C	-2.76039	0.21616	0.18332
C	-2.02836	1.19992	-0.56485
C	-2.01479	-0.38092	1.25637
C	-0.73573	1.5212	-0.27322
H	-2.48756	1.72116	-1.39584
C	-0.72318	-0.03514	1.52439
H	-2.46739	-1.12524	1.89999
H	-0.17927	2.26149	-0.83594
H	-0.15915	-0.47662	2.33765
C	-4.1316	-0.1408	-0.11699
C	-4.83171	-1.15878	0.58241
C	-4.88591	0.49976	-1.13522
C	-6.14764	-1.45996	0.25301
H	-4.35979	-1.72502	1.3778
C	-6.19919	0.11871	-1.38174
H	-4.4624	1.29796	-1.73455
H	-6.67029	-2.24435	0.79794
H	-6.76479	0.62067	-2.16502
N	-0.05415	0.92758	0.78051
C	1.36864	1.18327	0.99219
H	1.60311	2.17826	0.67611
H	1.59965	1.0754	2.03138
H	1.94517	0.48339	0.42414
C	-8.3118	-1.22556	-1.03301
H	-8.4688	-2.26026	-0.81018
H	-8.97324	-0.62874	-0.44039
H	-8.50651	-1.05061	-2.0705
N	-6.85363	-0.84715	-0.71344

Methylviologen dication (1b ion)

Charge = 1 Multiplicity = 2

C	-1.71347	-1.5493	-0.02243
C	-0.95798	-2.57366	0.54888
C	-2.93362	-1.18269	0.54536
C	-1.42293	-3.23166	1.68733
H	0.00356	-2.86296	0.10056
C	-3.39839	-1.84014	1.68473
H	-3.5291	-0.37524	0.09531
H	-0.8278	-4.03951	2.13733
H	-4.36026	-1.55059	2.13243
C	-1.20013	-0.82334	-1.27984
C	-1.95562	0.20102	-1.85114
C	0.02013	-1.18979	-1.8475
C	-1.4912	0.85827	-2.99025
H	-2.91796	0.48917	-1.40382
C	0.4853	-0.53178	-2.98638
H	0.61578	-1.99701	-1.39724
H	-2.08692	1.66526	-3.44099
H	1.44764	-0.82065	-3.4335
C	-3.15642	-3.59128	3.51277
H	-3.72874	-4.44711	3.22138
H	-3.77259	-2.92716	4.08214
C	0.24237	1.21799	-4.8156
H	-0.09684	2.23274	-4.80483
H	1.31215	1.19962	-4.82696
C	-0.29657	0.50991	-6.07249
C	-1.51016	0.91027	-6.63231
C	0.42856	-0.53159	-6.6513
C	-1.99875	0.26878	-7.77028
H	-2.08197	1.73089	-6.1753
C	-0.05957	-1.17273	-7.7902
H	1.38515	-0.84715	-6.21031
C	-1.27308	-0.77283	-8.34966
H	-2.95561	0.58388	-8.21123
H	0.51259	-1.9936	-8.24658
H	-1.65849	-1.27843	-9.24694

C	-1.95895	-4.04206	4.36978
C	-1.48111	-5.34889	4.26815
C	-1.35198	-3.14387	5.2475
C	-0.39699	-5.75756	5.0446
H	-1.96034	-6.05699	3.57663
C	-0.26689	-3.55222	6.02354
H	-1.72835	-2.11379	5.3276
C	0.21058	-4.85886	5.92234
H	-0.0207	-6.78778	4.96501
H	0.21174	-2.8437	6.7152
H	1.0654	-5.18129	6.5344
N	-2.64336	-2.86458	2.25568
N	-0.27018	0.49202	-3.55788

DFT Table. Orbital contour for the different dication - HOMO-1, HOMO, LUMO and LUMO-1

