

## **Extended Mechanistic Aspects on Photoinitiated Polymerization of 1,6-Hexanediol Diacrylate by Hexaarylbisimidazoles and Heterocyclic Mercapto Compounds**

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### ***UPLC-ESI-QTOF-MS Experiments***

Reaction products were analyzed by ultra performance liquid chromatography coupled to electrospray ionization quadrupole time-of-flight mass spectrometry (UPLC-ESI-QTOF-MS). On this account, diluted samples (1:50, v/v) were injected via full loop (loop volume: 2.5  $\mu$ L) onto an Acquinity UPLC system (Waters, Eschborn/Germany) mounted with a HSS T3 column (100 x 1.0 mm, particle size 1.8  $\mu$ m, Waters), and separated using a binary gradient; that is 0–1 min, isocratic 95% A (water / 0.1% formic acid), 5% B (acetonitrile / 0.1% formic acid); 1–16 min, linear from 5 to 95% B; 16–18 min, isocratic 95% B; 18–18.01, linear from 95 to 5% B; 18.01–20 min, isocratic 5% B. The flow rate was kept at 150  $\mu$ L/min during the entire analysis.

Eluting compounds were detected in positive and negative ionization mode from  $m/z$  50 – 1000 using a MicroTOF-Q I hybrid quadrupole time-of-flight mass spectrometer equipped with an Apollo II electrospray ion source (Bruker Daltonics, Billerica, MA, USA). Instrument parameters were defined as follows for the positive mode: nebulizer gas, nitrogen, 1.6 bar; dry gas, nitrogen, 6 L/min, 190°C; capillary, –5000 V; end plate offset, -500 V; funnel 1 RF, 200  $V_{pp}$ ; funnel 2 RF, 200  $V_{pp}$ ; in-source CID energy, 0 V; hexapole RF, 100  $V_{pp}$ ; quadrupole ion energy, 3 eV; collision gas, argon; collision energy, 3 eV; collision RF 200  $V_{pp}$ ; transfer time, 70  $\mu$ s; pre pulse storage, 5  $\mu$ s; spectra rate, 3 Hz. For the negative ionization mode all parameters were maintained except for the nebulizer gas (1.4 bar), capillary (4000 V), quadrupole ion energy (5 eV), collision energy (7eV), and collision RF (150  $V_{pp}$ ).

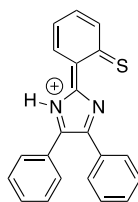
All mass spectra were acquired in centroid mode and recalibrated on the basis of lithium formate cluster ions after 20  $\mu$ L 10 mM lithium hydroxide 49.9/49.9/0.2 (dissolved in isopropanol/water/formic acid; v/v/v) were injected with the help of a diverter valve.

Reaction products were extracted by visual inspection of base peak chromatograms (isolation width:  $\pm$  0.02 Da) and identified on the basis of their accurate mass and their collision-induced dissociation (CID) mass spectrum. For acquisition of CID mass spectra quasi-molecular cluster ions were isolated at the Q1 (isolation width:  $\pm$  3) and fragmented inside the collision cell using argon as collision gas. Product ions were detected as already described.

### ***Characterization of photolysis products by UPLC-ESI-QTOF-MS***

LC-MS data of the starting material (**Ia**; **L-L**) and photolysis products (**P1–P4**; **P5a**; **P5b**) including elemental composition, retention time (rt), accurate mass and mSigma. The elemental composition of **P1–P4**; **P5a**; **P5b**; **L-L** corresponds to  $[M+H]^+$  type cluster ions and of **Ia** to  $[M-H]^-$  type cluster ions.

	Elemental Composition	Retention time (s)	calc $m/z$ (amu)	$m/z$ (amu)	$\Delta m$ (ppm)	mSigma	Relative abundance of $M+H+2$ (%)
<b>P1</b>	$C_{23}H_{18}N_5S^+$	408	396.128	396.124	10.1	66.7	8
<b>P2</b>	$C_{21}H_{16}ClN_2^+$	474	331.100	331.098	6	4	36
<b>P3</b>	$C_{21}H_{17}N_2^+$	434	297.139	297.137	6.7	6	9
<b>P4</b>	$C_{21}H_{14}ClN_2^+$	566	329.084	329.082	6.1	8.8	33
<b>P5a</b>	$C_{42}H_{30}ClN_4^+$	663	625.215	625.212	4.8	90.3	43
<b>P5b</b>	$C_{42}H_{30}ClN_4^+$	852	625.215	625.212	4.8	11	40
<b>Ia</b>	$C_2H_2N_3S^-$	30	99.996	99.997	-10	11.3	6
<b>L-L</b>	$C_{42}H_{29}Cl_2N_4^+$	900	659.176	659.178	-3	136.1	81



Chemical Formula:  $C_{21}H_{15}N_2S^+$

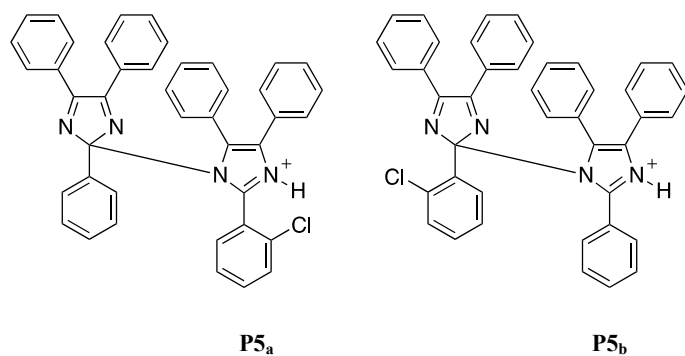
Exact Mass: 327,0950

Molecular Weight: 327,4217

$m/z$ : 327.0951 (100.0%), 328.0984 (22.7%), 329.0909 (4.5%), 329.1018 (2.5%), 330.0942 (1.0%)

Elemental Analysis: C, 77.03; H, 4.62; N, 8.56; S, 9.79

### Possible Structures of the isomers P5a and P5b



### Computational Details

The program package Spartan (available from Wavefunction, Inc.) was applied to calculate molecular orbitals. Density functional theory was chosen to obtain data applying B3LYP/6-31G\*. Spin density was calculated at the UB3LYP/6-31G\* level.

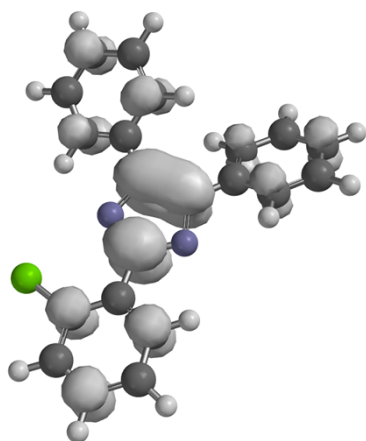


Figure S1: Spin density distribution of L•

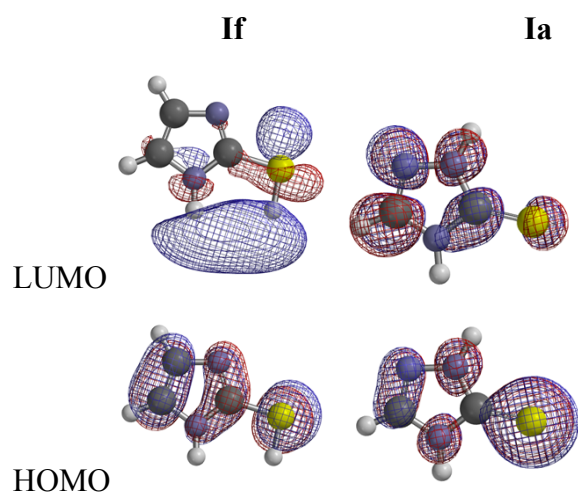


Figure S2: HOMO and LUMO patterns of **If** (thiol tautomer, left) and **Ia** (thione tautomer, right).

### Reactivity comparison of $L\cdot$ with mercapto compounds

1 mol% *o*-Cl HABI was dissolved in 2.3 g HDDA (inhibitor was previously removed by basic  $Al_2O_3$ ). The solution obtained was exposed in a 1 cm quartz cuvette using a Hg–Xe 200 W UV lamp (LOT-Oriel) in combination with a water filter and a 320–380 nm broadband filter to generate lophyl radicals. The solution was continuously stirred during exposure. 0.2 g of HDDA were added comprising the mercapto compound, which had a concentration of 6.7 mol% in the final solution. The absorbance was monitored using the same fiber optical spectrometer setup. All solutions were purged with nitrogen for 15 min before exposure started. Figure S3 shows the time traces in the case of addition of **Ia** and **II**.

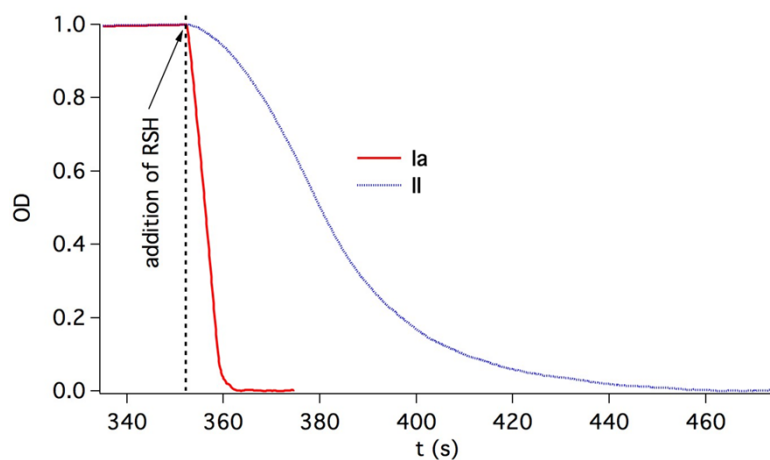


Figure S3: Normalized Optical density (OD) of  $L\cdot$  obtained during exposure with UV light. A mercapto compound (**Ia** or **II**) was added after an irradiation time when no significant change of OD occurs. The lamp was turned on during the entire measurement.

Change of the solvent resulted in the time traces shown in Figure S4 decaying faster in DMSO compared to HDDA considering the system  $L\cdot$ /**II**.

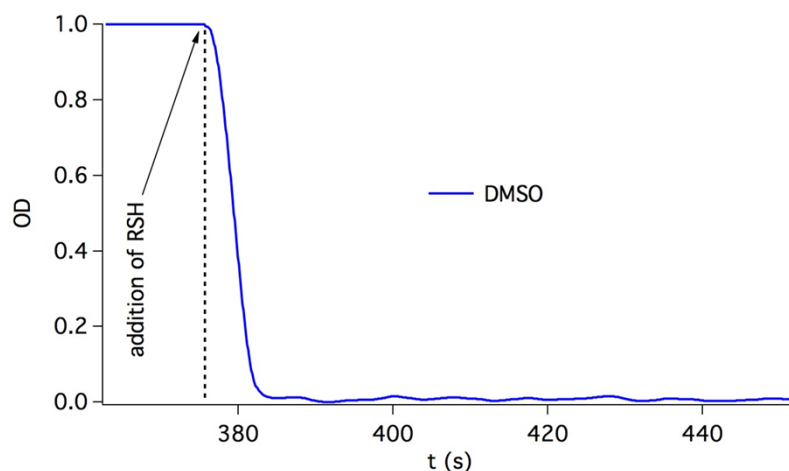


Figure S4: Normalized Optical density (OD) of  $L\cdot$  obtained during exposure with UV light measured in DMSO. The mercapto compound **II** was added after an irradiation time when no significant change of OD occurs. The lamp was turned on during the entire measurement.

***Formation of insoluble polymer after irradiation in the photo-DSC Setup***

1-mol% o-Cl-HABI and 6,7 mol% RSH were exposed in the photo-DSC. After exposure, the sample was extracted with MEOH and the amount on insoluble polymer was gravimetrically determined. Table S2 summarizes the results. Exposure times correspond to the time when the maximum of polymerization reached in case of Ia (1.8 s) and II (61.2 s).

Table S2

Mercapto compound	Exposure time (s)	Yield on insoluble polymer (%)
Ia	1.8	100
II	1.8	0
Ia	61.2	100
II	61.2	15