

Supporting Information

Photoinitiators from bio-sourced naphthoquinone – The application of naphthoquinone based Vitamins K1 and K3 in free radical photopolymerization

Timur Borjigin^{1,2}, Ji Feng^{1,2}, Michael Schmitt^{1,2}, Di Zhu³, Fabrice Morlet-Savary^{1,2*}, Pu Xiao^{4*}, Jacques Lalevée^{1,2*}

¹Université de Haute-Alsace, CNRS, IS2M UMR 7361, F-68100 Mulhouse, France

²Université de Strasbourg, F-67000 Strasbourg, France

³Research School of Chemistry, Australian National University, Canberra, ACT 2601, Australia

⁴State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, P. R. China

Chemical Compounds Used in This Work

The vitamin K1 (phylloquinone), K3 (menadione), and juglone were purchased from Sigma-Aldrich Inc (St. Louis, US). The iodonium salt (i.e., bis(4-tert-butylphenyl)iodonium hexafluorophosphate, noted Iod or Speedcure 938) and the tertiary amine (ethyl 4-dimethylaminobenzoate, EDB) used in the different photoinitiating systems, were purchased from Lambson Ltd (Leeds, UK). Trimethylolpropane triacrylate (TMPTA) and polyethylene glycol diacrylate (PEGDA) were obtained from Allnex (Frankfurt am Main, Germany). The above reagents were used without further purification.

Electrochemical Measurements and Free Energy Changes Calculations

The oxidation (E_{ox}) and reduction (E_{red}) potentials were studied by cyclic voltammetry (Voltalab 6; Radiometer). The naphthoquinone-imidazolyl derivatives were co-dissolved with tetrabutylammonium hexafluorophosphate (as the supporting electrolyte) in dichloromethane. The working electrode was a platinum disk and a saturated calomel electrode ($-SCE$) was used as the reference; all potentials were determined from half-peak potentials. The free energy changes from the singlet state

(ΔG_{Iod}^{S1} or ΔG_{EDB}^{S1}) for the electron transfer reaction were determined with E_{ox} , E_{red} , and E_{S1} . The specific calculation formula is detailed in Equations (1) and (2). In the same way that Equations (3) and (4) show the specific calculations regarding the free energy change from the triplet state (ΔG^{T1}). The value of the triplet state energy level (E_{T1}) was calculated by molecular modeling (Gaussian 16 suite of programs). In the literature, the reduction potential of the iodonium salt is -0.7 V, while the oxidation potential of EDB is 1.0 V.

$$\Delta G_{Iod}^{S1} = E_{ox} - (-0.7eV) - E_{S1} \#(1)$$

$$\Delta G_{EDB}^{S1} = 1eV - E_{red} - E_{S1} \#(2)$$

$$\Delta G_{Iod}^{T1} = E_{ox} - (-0.7eV) - E_{T1} \#(3)$$

$$\Delta G_{EDB}^{T1} = 1eV - E_{red} - E_{T1} \#(4)$$

Table S1. Light absorption properties of the Juglone, K1 and K3: maximum absorption wavelengths (λ_{max}); extinction coefficients at λ_{max} (ϵ_{max}) and extinction coefficients at the emission wavelength of the LED@405 nm ($\epsilon_{405\text{ nm}}$).

	λ_{max} (nm)	ϵ_{max} ($M^{-1} * cm^{-1}$)	ϵ_{405nm} ($M^{-1} * cm^{-1}$)
Juglone	430	8980	7700
K1	333	15200	620
K3	335	9200	180

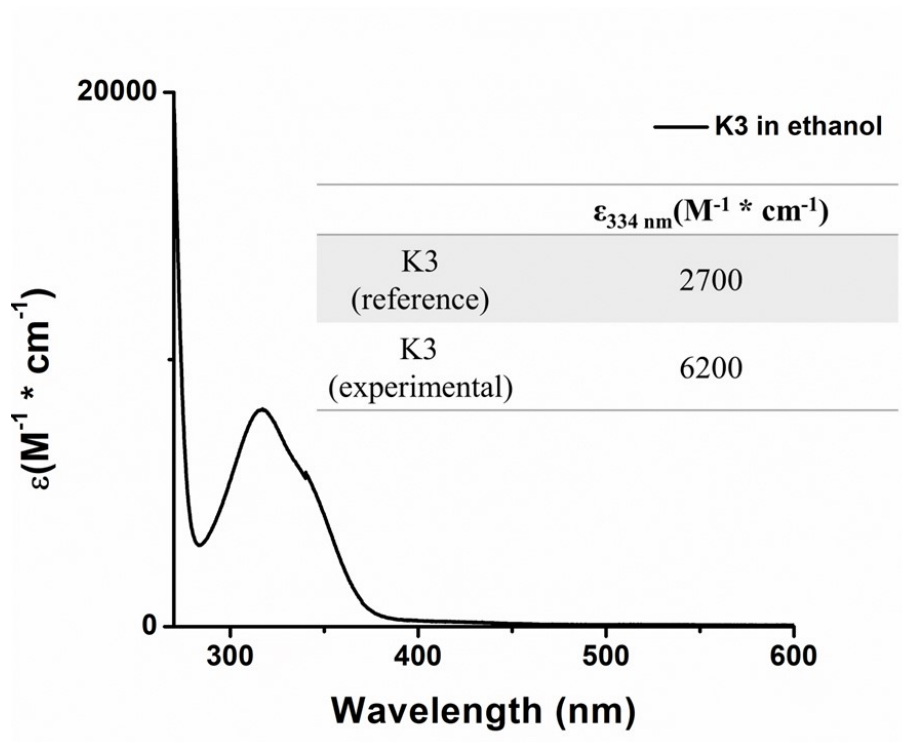


Figure S1. UV-vis absorption of K3 in ethanol.

Table S2. The final conversions (FC) of acrylate functional groups of TMPTA and PEGDA using different PISs.

PISs	FCs (%)	
	TMPTA	PEGDA
Juglone	0	Not measured
K1	20	0-1
K3	0-2	83
Juglone + Iod	0	Not measured
K1 + Iod	59 ^a	65 ^a
K3 + Iod	0	93
Iod + EDB	90 ^b	90 ^b
Juglone + EDB	21	Not measured
K1 + EDB	48	8
K3 + EDB	63	85
Juglone + Iod + EDB	38	Not measured
K1 + Iod + EDB	79	81 ^a
K3+ Iod + EDB	83	95

^a Slopes, Figure 3 indicates an overlapping of at least 2 different mechanisms.

^b Inhibition period could be observed.

Table S3. The pictures of samples before and after polymerization.

	Before	After
Juglone		Liquid
K1		
K3		Liquid
Juglone + Iod		Liquid
K1 + Iod		
K3+ Iod		Liquid
Juglone + EDB		
K1 + EDB		
K3 + EDB		
Juglone + Iod + EDB		
K1 + Iod + EDB		
K3 + Iod + EDB		

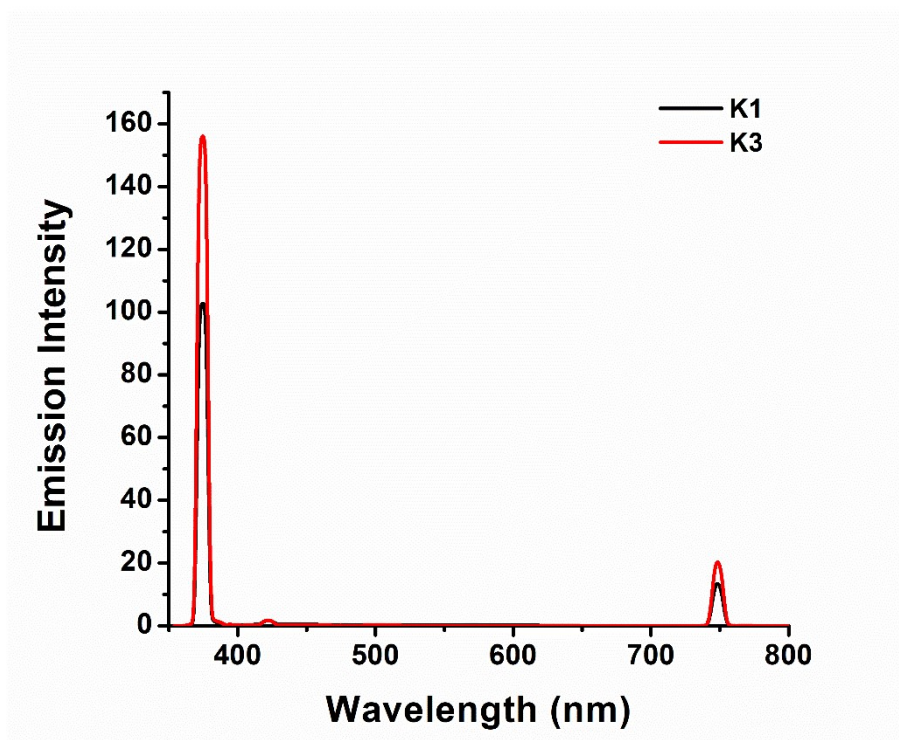
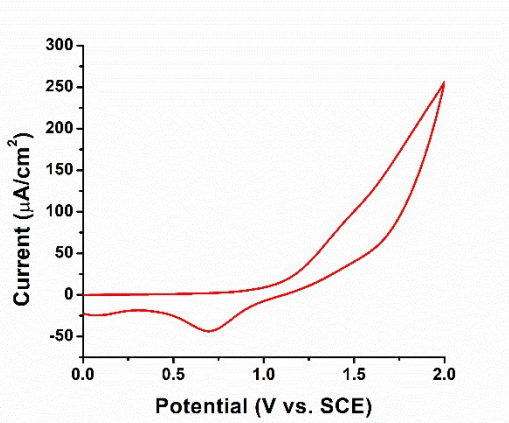
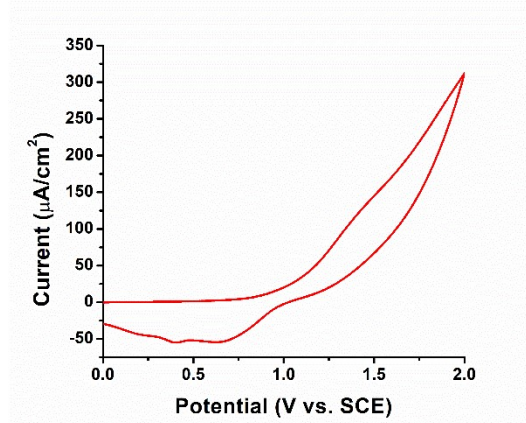


Figure S2. Fluorescence spectrum of K1(10^{-4} M) and K3 (10^{-4} M) in dichloromethane.

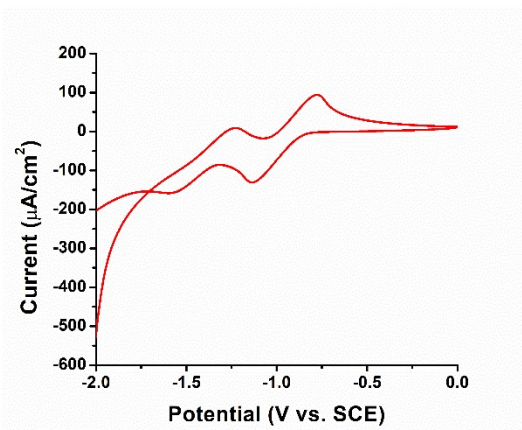
No fluorescence could be observed, the signals are due to the instrument's line filter



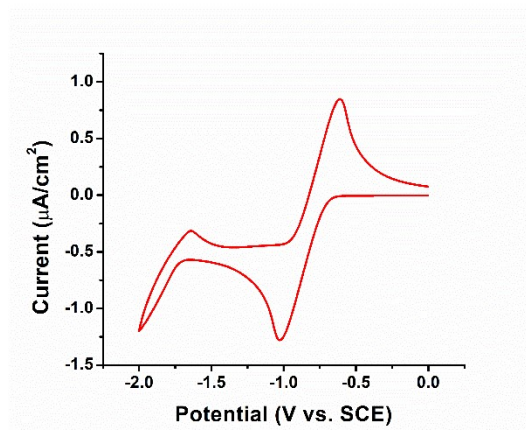
(a)



(b)

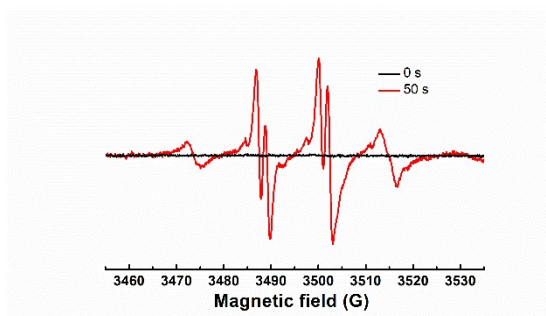


(c)

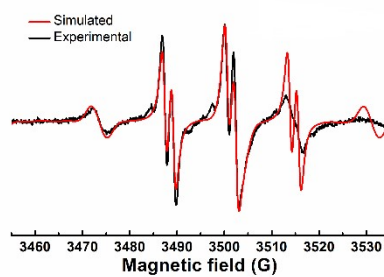


(d)

Figure S3. Cyclic voltammetry curves for oxidation of (a) K1 and (b) K3; Cyclic voltammetry curves for reduction of (c) K1 and (d) K3.



(a)



(b)

Figure S4. ESR-ST spectra of the radical adducts obtained in the presence of K3/PEGDA (a) before and after irradiation, and (b) experimental (black) and simulated (red) spectra after irradiation; LED@405 nm.