## SUPPORTING INFORMATION

## Picosecond pulse radiolysis of the liquid diethylcarbonate

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**Figure S1.** Comparison of absorbance decays at 630 nm of the solvated electron in neat methanol and in solutions of DEC in methanol at 0.01 and 1 mol L<sup>-1</sup>. The absence of influence of DEC on the decay indicates that no reaction occurs between  $e_{CH3OH}$  and DEC. This feature supports the possible solvation of the electron, without attachment, in neat DEC.



**Figure S2.** Comparison between the simultaneous decays at long time in neat DEC of the absorbances at 330 nm assigned to DEC(+H)<sup>-</sup> and at 600 nm assigned to DEC(-H)<sup>-</sup>. Note that until 150 ns the absorbance at 600 nm contains in addition a component assigned to  $e_{DEC}^{-}$ . Streak camera detection. Optical path: 1 cm.



**Figure S3.** Pseudo-first order decay of solvated electron at 1200 nm in  $5 \times 10^{-2}$  mol L<sup>-1</sup> HClO<sub>4</sub> solution compared to the decay in neat DEC.



**Figure S4.** Pseudo-first order decay of solvated electron absorbance at 1200 nm in DEC solution with  $10^{-2}$  mol L<sup>-1</sup> acetone compared to the decay in neat DEC. Inset: Pseudo-first decay of solvated electron absorbance at 1200 nm in 0.5 mol L<sup>-1</sup> acetone solution.



**Figure S5.** Transient optical absorption spectrum in DEC solutions with  $5 \times 10^{-2}$  mol L<sup>-1</sup> biphenyl at 550 ps. It is constituted of the sum of two components, *i.e.* the intense spectrum of the Ph<sub>2</sub><sup>-</sup> anion radical and, for a small part, the spectrum of DEC(-H)<sup>-</sup>.



**Figure S6.** Variation of the observed pseudo-first-order rate constant of the  $Ph_2^{-}$  formation in the scavenging reaction of solvated electrons by biphenyl *versus* the biphenyl concentration. Data of  $k_{obs}$  are obtained from the second-step increase of  $Ph_2^{-}$  observed at 630 nm after the absorption of the radical DEC(-H) has been subtracted.



**Figure S7.** Formation and decay kinetics at 410 nm in DEC solutions of biphenyl at variable concentrations. Each signal is constituted of the sum of two components, that of the anion radical  $PH_2^{-1}$  and that of the radical DEC(-H)<sup>2</sup>. Pulse duration : 5 ps, dose : 50 J L<sup>-1</sup>.



**Figure S8.** Decay kinetics at 635 nm in DEC solutions of biphenyl at variable concentrations. Each signal is constituted of the sum of two components, that of the anion radical  $PH_2^{-1}$  and that of the radical DEC(-H)<sup>-</sup>. Pulse duration : 5 ns, dose : 500 J L<sup>-1</sup>.



**Figure S9.** Time evolution of the absorbance at the biphenyl concentration in DEC of  $10^{-2}$  mol L<sup>-1</sup> close to the first isosbestic wavelength between the spectra of  $e_{DEC}$  and  $Ph_2$ . (540 nm). Note that, for clarity, the signals are shifted on the ordinates scale.



**Figure S10.** Time evolution of the absorbance at the biphenyl concentration in DEC of  $10^{-2}$  mol L<sup>-1</sup> close to the second isosbestic wavelength between the spectra of  $e_{DEC}$  and  $Ph_2^{-}$  (720 nm). Note that, for clarity, the signals are shifted by 0.2 units on the ordinates scale.



**Figure S11.** Time evolution of the absorbance at the biphenyl concentration in DEC of 1 mol  $L^{-1}$  close to the isosbestic wavelength between the spectra of  $e_{DEC}$  and  $Ph_2^{-}$  (540 nm), and at the maximum wavelength of  $Ph_2^{-}$  (640 nm). Shift by 0.1 unit on the ordinates scale.