

# CHEMPHYSICHEM

## Supporting Information

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### **Photoinduced Biphasic Hydrogen Evolution: Decamethylsmocene as a Light-Driven Electron Donor**

Peiyu Ge,<sup>[a]</sup> Astrid J. Olaya,<sup>[a]</sup> Micheál D. Scanlon,<sup>[a]</sup> Imren Hatay Patir,<sup>[b]</sup> Heron Vrubel,<sup>[c]</sup> and  
Hubert H. Girault\*<sup>[a]</sup>

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[a] *P. Ge, A.J. Olaya, Dr. M.D. Scanlon and Prof. H.H. Girault*

*Laboratoire d'Electrochimie Physique et Analytique (LEPA)*

*Ecole Polytechnique Fédérale de Lausanne (EPFL)*

*Station 6, CH-1015 Lausanne (Switzerland)*

*Fax: (+)41 (0)21 693 36 67*

*E-mail: Hubert.Girault@epfl.ch*

[b] *Dr. I. Patir Hatay*

*Department of Chemistry*

*Selcuk University*

*42031 Konya (Turkey)*

[c] *H. Vrubel*

*Laboratory of Inorganic Synthesis and Catalysis (LISC)*

*Ecole Polytechnique Fédérale de Lausanne (EPFL)*

*BCH 3305, Av. Forel 2, CH-1015 Lausanne (Switzerland)*

**Determination of the interfacial Galvani potential difference and equilibrium concentrations of electrolyte ions for a shake flask on initially contacting the aqueous and organic phases**

Taking into account the Nernst equation for the distribution of all common ions, the mass balance of all ions in both phases and the electroneutrality condition for both phases, the following equation may be arrived at (as derived in the Supporting Information of several recent publications)<sup>[1-3]</sup>

$$\sum_i z_i F c_i^w = \sum_i \frac{z_i F c_{i,\text{total}}}{1 + \frac{V^\circ}{V^w} \exp\left[\frac{z_i F}{RT} (\Delta_\circ^w \phi - \Delta_\circ^w \phi_i^0)\right]} \quad (\text{s1})$$

where  $\Delta_\circ^w \phi_i^0$  is the formal ion transfer potential of species  $i$ ,  $V^w$  and  $V^\circ$  are the water and oil phase volumes, respectively,  $c_{i,\text{total}}$  and  $c_i^w$  are the initial total concentration of  $i$  present prior to equilibrium and the concentration of  $i$  in the aqueous phase at equilibrium, respectively, and all other terms have their usual meanings.

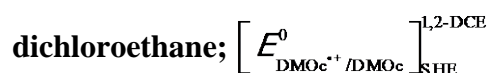
Using Equation (s1), the initial partition of the individual electrolyte ions in the biphasic system outlined in Scheme 1(A), main text, established an interfacial Galvani distribution potential ( $\Delta_\circ^w \phi$ ) of 0.504 V for all common ions at equilibrium. The calculation was performed using Mathematica Software (version 7.0), see Table S1.

**Table S1.** Calculated equilibrium concentrations (mM) of each of the constituent electrolyte ions for the shake-flask outlined in Scheme 1(A), main text, (aqueous phase of 100 mM HCl and 5 mM LiTB-DEE; organic phase of 2.5 mM DMOc and 5 mM BATB in 1,2-DCE) for the initial partition of the electrolyte ions.<sup>[A]</sup>

Partitioning ion	$\Delta G_{tr,j}^{0,o \rightarrow w}$ (kJ·mol <sup>-1</sup> )	$\Delta_o^w \phi_{tr,j}^0$ V	Aqueous	1,2-DCE
[H <sup>+</sup> ] <sub>eq</sub> / mM	-56.0	0.58	95.028	4.972
[Li <sup>+</sup> ] <sub>eq</sub> / mM	-62.7	0.64	4.975	0.025
[BA <sup>+</sup> ] <sub>eq</sub> / mM	67.5	-0.70	2.20×10 <sup>-20</sup>	5
[TB <sup>-</sup> ] <sub>eq</sub> / mM	68.5	0.71	0.003	9.997
[Cl <sup>-</sup> ] <sub>eq</sub> / mM	-51.1	-0.53	100	3.292×10 <sup>-16</sup>

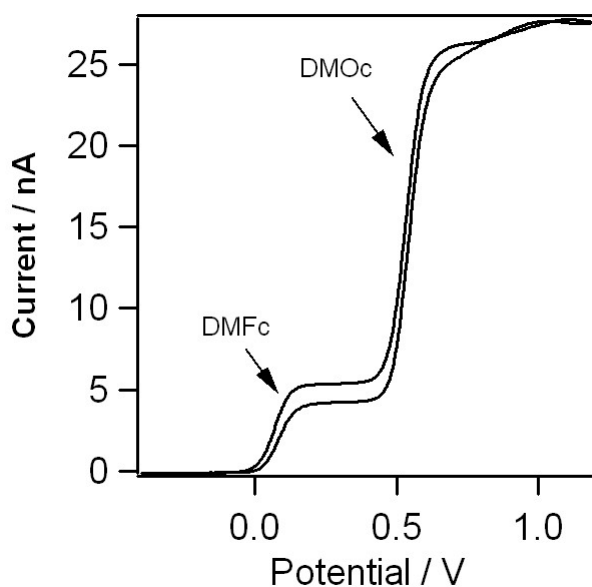
<sup>[A]</sup> The Galvani potential difference ( $\Delta_o^w \phi$ ) is calculated as 0.504 V for the initial partition of the electrolyte ions. The Gibbs energy of transfer ( $\Delta G_{tr,j}^{0,o \rightarrow w}$ ), and consequently the standard ion transfer potential ( $\Delta G_{tr,j}^{0,o \rightarrow w} = -z_j F \Delta_o^w \phi_{tr,j}^{0,o \rightarrow w}$ ), for each electrolyte ion were obtained from references <sup>[4]</sup> and <sup>[5]</sup>, respectively.

## Determination of the Ground State Redox Potential of Decamethylsmocene in 1,2-



### Microelectrode Experiments.

2-electrode voltammetry measurements in organic media were carried out on a CHI 900 potentiostat (CH Instruments, Texas, U.S.A.) using a platinum disk microelectrode ( $\varnothing = 25 \mu\text{m}$ ) and a silver wire as the working and quasi-reference electrodes, respectively. A scan rate of  $20 \text{ mV}\cdot\text{s}^{-1}$  was employed and the potential expressed vs. the standard hydrogen electrode (SHE) in 1,2-DCE<sup>[6]</sup> using decamethylferrocene (DMFc) as an internal standard for calibration (the standard redox potential of DMFc vs. SHE in 1,2-DCE,  $\left[ E_{\text{DMFc}^{+}/\text{DMFc}}^0 \right]_{\text{SHE}}^{1,2\text{-DCE}}$ , is 0.04 V).<sup>[7]</sup> The background electrolyte was 5 mM BATB.



**Figure S1.** Cyclic voltammogram of 5 mM DMOc in 1,2-DCE using a platinum disk microelectrode ( $\varnothing = 25 \mu\text{m}$ ). Potentials (V) are expressed vs. SHE using DMFc as a

calibration standard.  $\left[ E_{\text{DMOc}^{+}/\text{DMOc}}^0 \right]_{\text{SHE}}^{1,2\text{-DCE}} = 0.48 \text{ V}$ .

## Apparent Quantum Yield Calculations

The biphasic shake flask was illuminated using a high-powered LED with a wavelength ( $\lambda$ ) of 365 nm.

The energy of a single photon at 365 nm is:

$$E = \frac{hc}{\lambda} = \frac{(6.63 \times 10^{-34})(2.99 \times 10^8)}{365 \times 10^{-9}} = 5.4 \times 10^{-19} \text{ J}$$

where  $h$  is Planck's constant and  $c$  is the speed of light in vacuum.

The total power adsorbed from the LED (measured using a photodiode power sensor) was 0.15 W and the experiment was carried out for 24080 s. Therefore, the total energy adsorbed during the course of the reaction was 3612 J.

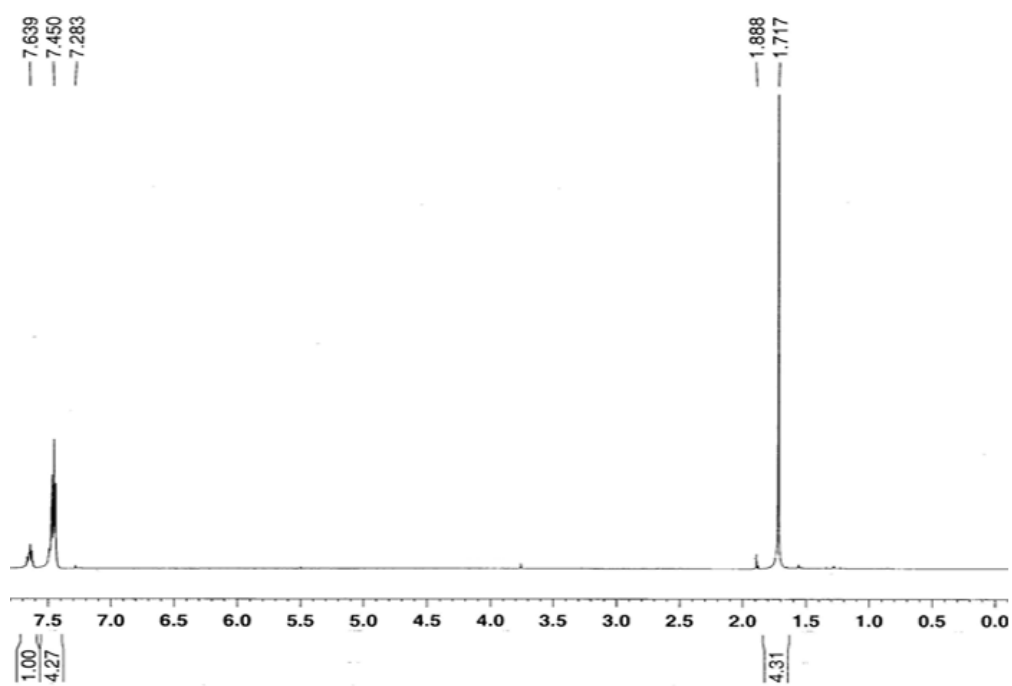
Thus, the total “*number of incident photons*” was  $6.7 \times 10^{21}$ .

The quantity of hydrogen evolved during the reaction was 2.88  $\mu\text{mol}$ . Based on the stoichiometry of the reaction, see Equation (3), main text, two moles of DMOc are consumed to produce one mole of  $\text{H}_2$ .

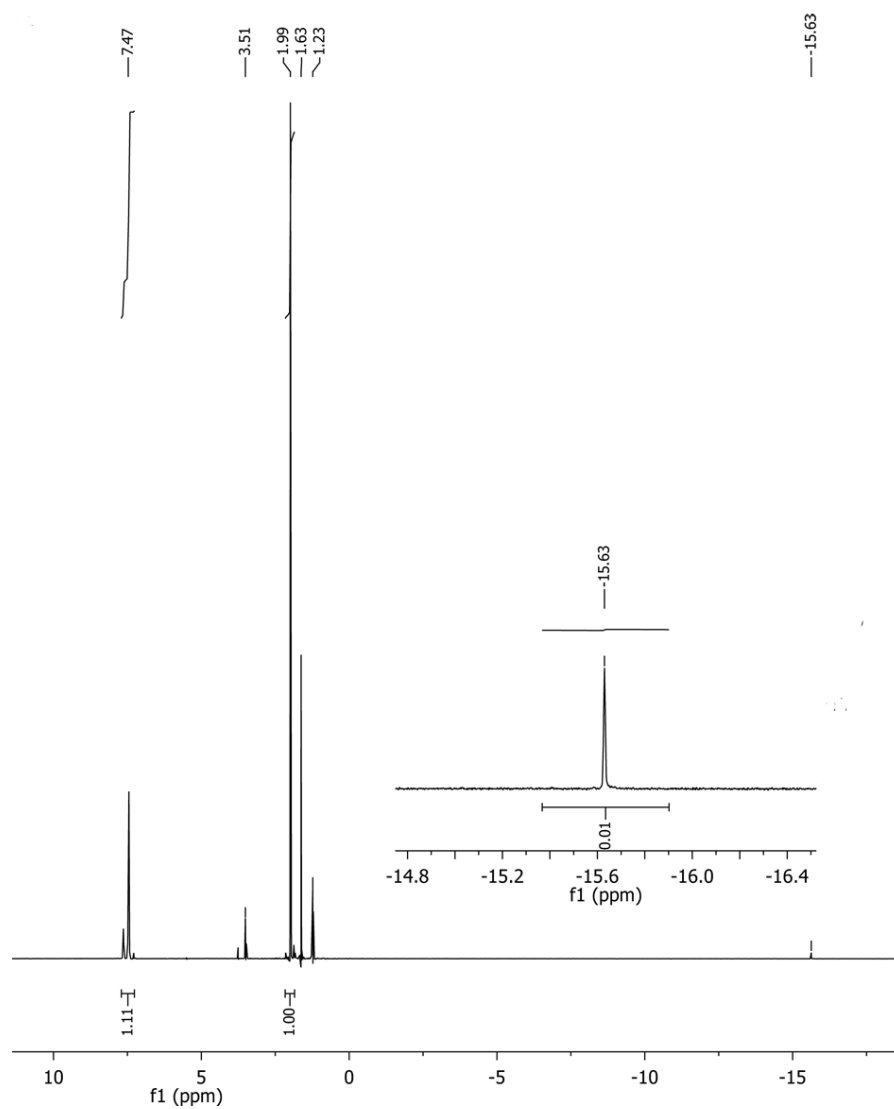
Therefore, the number moles of DMOc reacted was 5.76  $\mu\text{mol}$  and the “*number of reacted electrons*” or DMOc molecules oxidised, taking Avogadro's constant as  $6.022 \times 10^{23} \text{ mol}^{-1}$ , was  $3.4687 \times 10^{18}$ .

Using Equation (6), main text, the Apparent Quantum Yield was calculated as 0.052 %.

# $^1\text{H}$ NMR studies

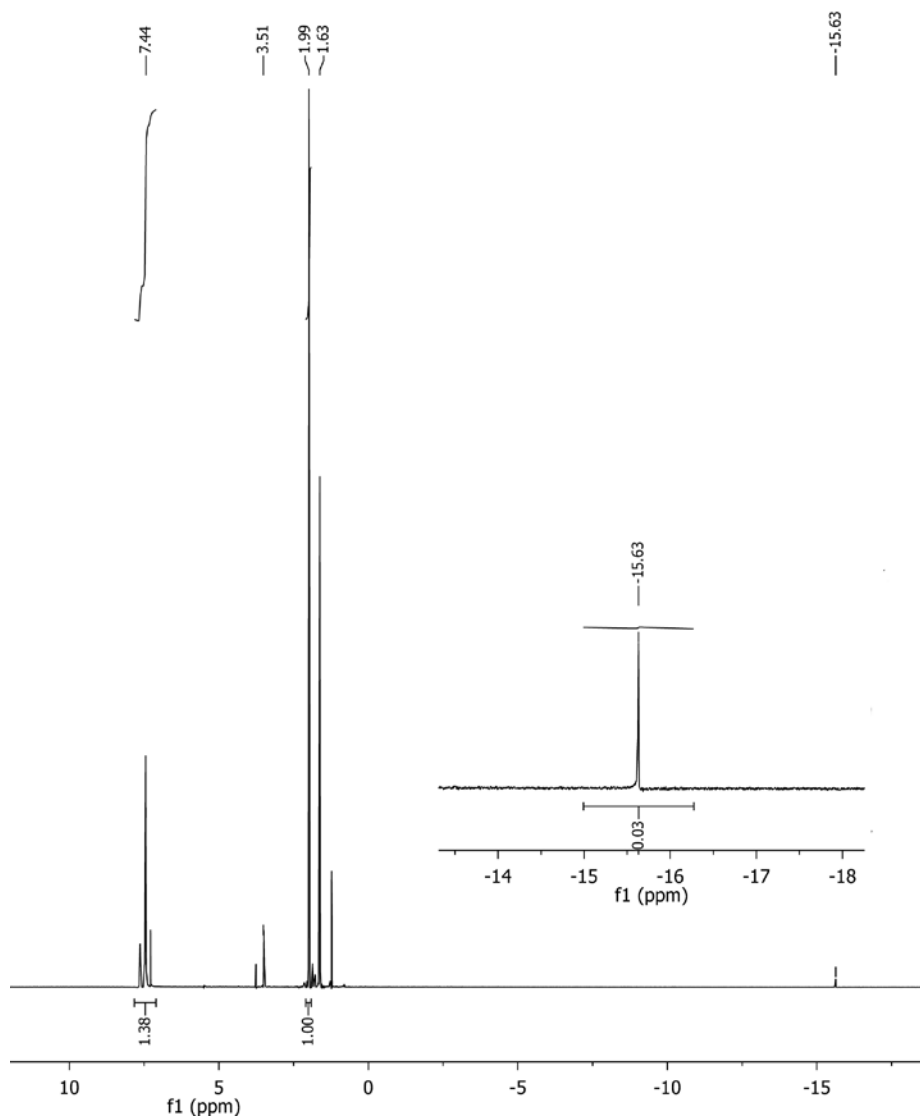


**Figure S2.**  $^1\text{H}$  NMR of 5 mM DMOc and 5 mM BATB in  $\text{CDCl}_3$  solvent.

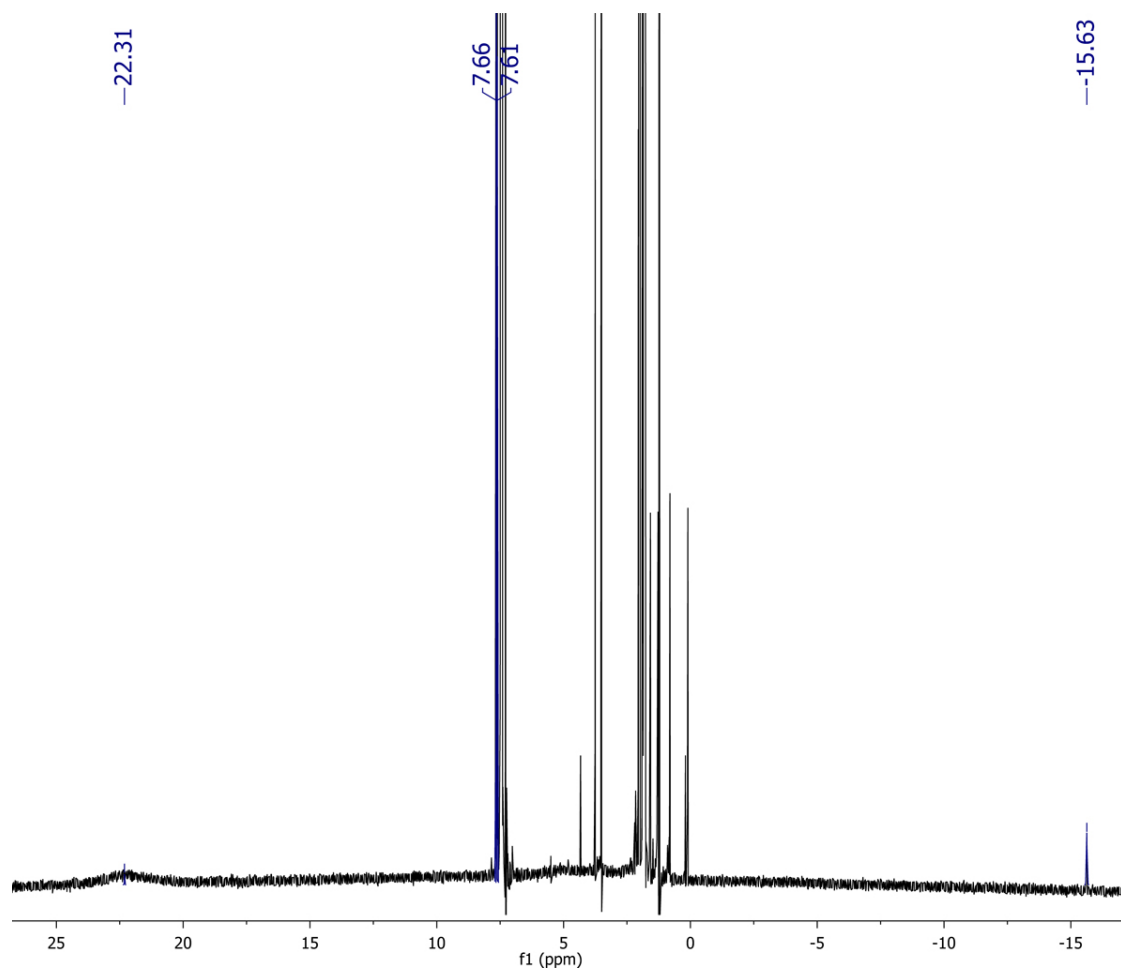


**Figure S3.**  $^1\text{H}$  NMR of the organic phase after a shake flask reaction with the composition in Scheme 1(B) for 30 min. in the dark.



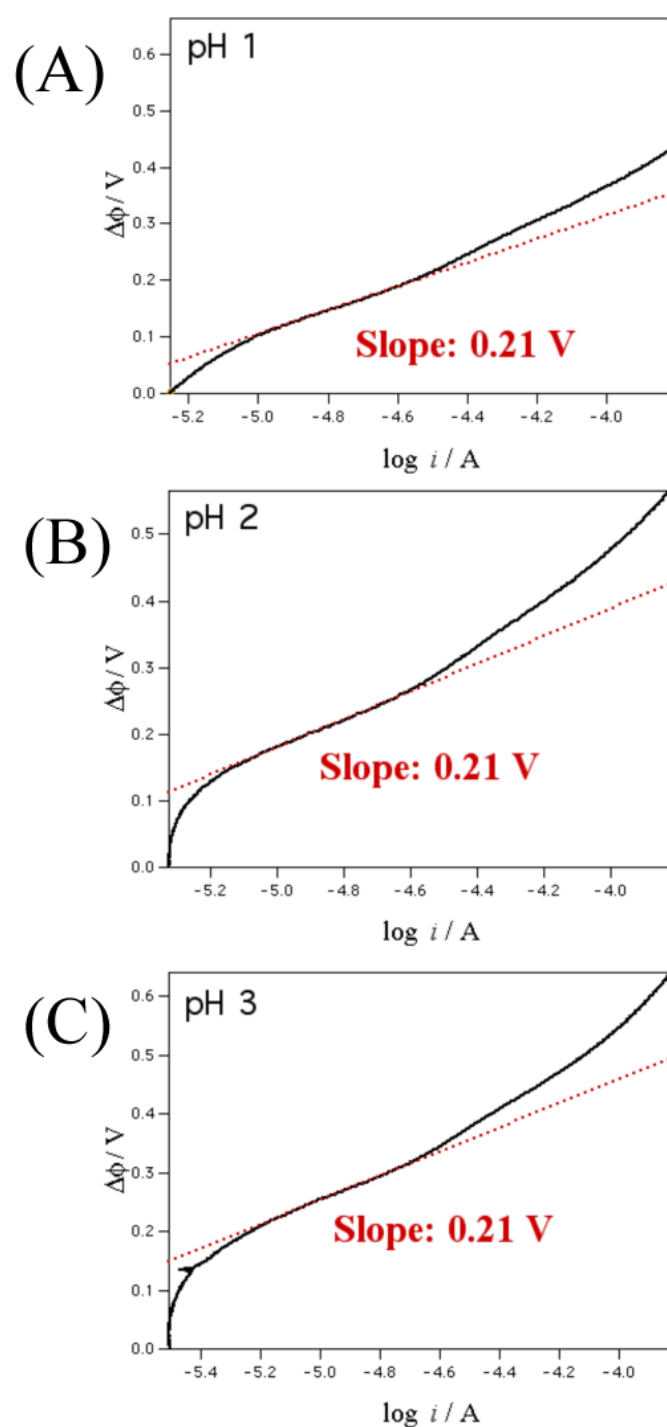


**Figure S4.**  $^1\text{H}$  NMR of the organic phase after shake flask reaction with the composition in Scheme 1(B) for 30 min. under white light illumination.



**Figure S5.**  $^1\text{H}$  NMR of 5 mM DMOc in  $\text{CDCl}_3$  containing 5 mM HTB after one-phase reaction under white light illumination (i.e. evidence of the peak at 22 ppm)

## Tafel Slope Analysis of 4-Electrode Voltammetry Data for Decamethylsmocene



**Figure S6.** A Tafel analysis was performed on each of the forward (negative to positive direction) sweeps of DMOc at pH 1, 2 and 3 from the CV data shown in Fig. 5(A), main text. At each pH a Tafel slope of 1/210 mV was observed indicating an apparent transfer coefficient of ca. 0.35.

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