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Solid state electrochemiluminescence from homogeneous and patterned monolayers of bifunctional spirobifluorene

Sergej Kudruk,[a] Elena Villani,[b] Federico Polo,[c] Sebastian Lamping,[a] Martin Körsgen,[d] Heinrich F. Arlinghaus,[d] Francesco Paolucci,[b] Bart Jan Ravoo,[a] Giovanni Valenti,*[b] and Fabio Rizzo*[a,e]

Electrochemiluminescence (ECL) generated by a monolayer of spirobifluorene derivative covalently bound onto an indium tin oxide (ITO) substrate is reported for the first time. Our approach allows to efficiently prepare homogeneous and patterned substrates through micromolding in capillaries (MIMIC), and opens novel scenarios for multicolour ECL applications.

Electrochemiluminescence (ECL) is the electrochemical activation of suitable molecules or ions to generate, upon sufficiently exergonic electron transfer reactions, excited state species (emitters) that cause luminescence. ECL is a very attractive analytical tool due to low background and high sensitivity.[1] Since its early studies, an increasing number of research activity was dedicated to study novel efficient ECL dyes for multicolour sytems.[2] Compared to the ECL in homogeneous solution, where the emitters are dissolved and free to diffuse, the development of the heterogeneous ECL, where emitters are confined at the electrode surface, emphasizes the good temporal and spatial resolution of the technique while minimizing or avoiding some drawbacks, such as the experimental design and the regeneration of species.[3] Heterogeneous ECL has recently been proposed for the highly sensitive detection of different analytes in complex matrixes, such as proteins in latent fingermarks,[4] the quantification of cancer biomarkers[5] and more recently single cell visualization.[6] To date, inorganic coordination complexes such as ruthenium(II) tris-bipyridine[7] are the most widely used luminophores for the heterogeneous ECL systems since they provide very intense signals. However, the main drawback is

that the red ECL emission cannot be tuned, thus hampering its application in multi-coloured systems. As an alternative, other transition metals, e.g. iridium[8] and platinum,[9] or nanomaterials such as quantum dots[10] or doped silica nanoparticles[11] are employed to tune the ECL emission. Although organic molecules offer an easy possibility to vary the emission wavelength thanks to their chemical versatility,[12] their use in heterogeneous ECL is rare.[13] Recently, the high efficient electrochemiluminescent properties of bifunctional organic dyes based on spirobifluorene unit chemically modified with two triarylamine units (Spiro-TPA) were described.[12a,14] Translating the ECL emission of organic dyes from solution to solid state is of enormous interest. Moreover, although spirobifluorenes are attracting a lot of interest in many technological applications,[15] the formation of controlled ordered monolayers of spirobifluorene derivatives covalently linked to solid support is rare.[16]

Herein, we present the fabrication and the electrochemical, photophysical and ECL characterizations of the organic emitter **1**, a derivative of Spiro-TPA (Chart 1), investigated either in solution or as self-assembled monolayer (SAM) onto an indium tin oxide (ITO) electrode surface. Our synthetic approach involves the independent functionalization of the two fluorene halves to favour the covalent linkage of the chromophore onto the ITO surface in packed monolayer.

Compound **1** was prepared as depicted in Scheme S1 (for experimental details see the Electronic Supplementary Information, ESI). Friedel-Craft acylation of 2,7-dibromo-9,9'-spirobifluorene (**2**) allowed to introduce a ketone on the unsubstituted fluorene half (**3**). The intermediate **4**, obtained by Baeyer-Villiger reaction, was deprotected by reaction with boron tribromide to give the 2-hydroxy-2',7'-dibromo-9,9'-spirobifluorene (**5**). The Suzuki cross-coupling reaction gave the extended aromatic compound **6** bearing two triphenylamine substituents. Then, the linker was added by reaction with (3-isocyanatopropyl)triethoxysilane to give the final product **1**.

[a.] Organic Chemistry Institute and CeNTech, Westfälische Wilhelms-Universität Münster, Corrensstrasse 40, 48149 Münster, Germany.

[b.] Department of Chemistry "G. Ciamician", University of Bologna, via Selmi 2, 40126 Bologna, Italy. Email: g.valenti@unibo.it

[c.] National Cancer Institute-CRO Aviano, via F. Gallini 2, 33081 Aviano, Italy.

[d.] Physics Institute, Westfälische Wilhelms-Universität Münster, Wilhelm-Klemm-Strasse 10, 48149 Münster, Germany.

[e.] Institute of Molecular Science and Technologies (ISTM) National Research Council (CNR) and INSTM, via Golgi 19, 20133 Milano, Italy. Email: fabio.rizzo@cnr.it
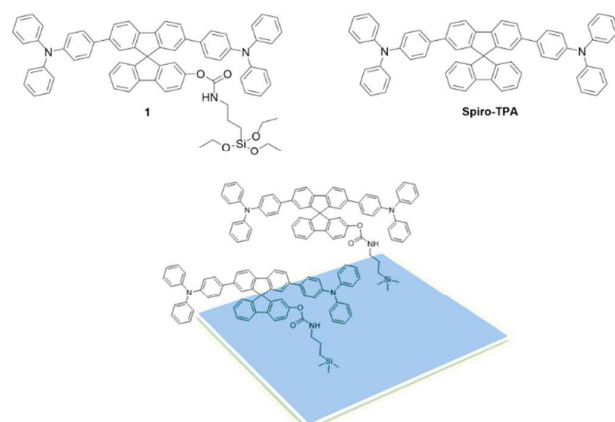
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Chart 1. Chemical structure of dye **1** and its binding mode onto solid surface. The structure of Spiro-TPA is reported for comparison.

Figure 2. a) Non functionalized ITO vs. functionalized ITO in XPS analysis of nitrogen signal. b) TOF-SIMS overlay of signals in positive mode. c) and d) Fluorescence microscopy on patterned ITO substrate (lines 50x30 and 25x15 µm).

The photophysical characterization of **1** in DMF solution (Figure 1a) shows the same trend reported for Spiro-TPA (Figure S1 and Table S1). The absorption spectrum displays two bands in the UV region with the lower peak at 372 nm attributed to the π-π* transition of the aromatic system,[12a,14] while the photoluminescent (PL) spectrum shows a structureless broad band with maximum at 456 nm.

Not unexpectedly, the comparison between the two spiro-derivatives indicates that the presence of the linker is not significantly affecting the optical properties of the dye, in line with the well-known lack of electronic conjugation between the two fluorene halves in spirobifluorene-based molecules.[17]

SAM of **1** on ITO coated glass was obtained by immersing for 24h freshly cleaned substrates in a 0.5 mM solution of **1** in toluene, at room temperature and under argon atmosphere. Subsequently, the functionalized substrates were rinsed thoroughly with toluene, dichloromethane and ethanol and dried under an argon stream.

Characterization of the functionalized surfaces by X-ray photoelectron spectroscopy (XPS) revealed the presence of peaks associated with tertiary amine at 400 eV and amide at 402 eV, which are absent in the cleaned solid support (Figure 2a and S2).

By static water contact angle measurements, the increased values from 54.5° (unfunctionalized ITO) to 76.5° (functionalized ITO) indicates the increased hydrophobicity of the surface in presence of SAM (Figure S3).
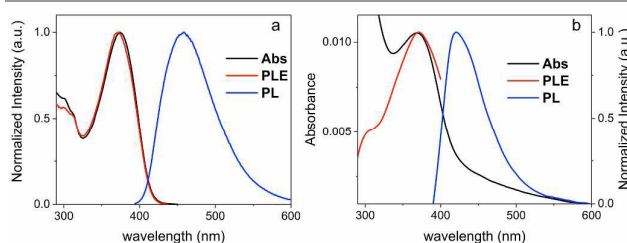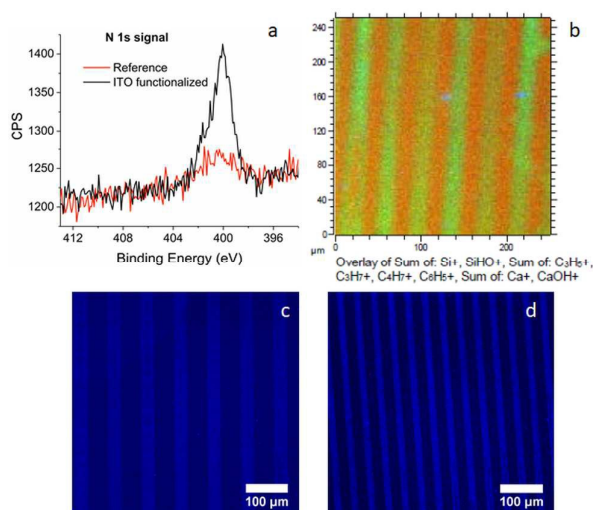
Further analyses of the organic monolayer were performed on patterned SAM obtained by micromolding in capillaries (MIMIC),[18] which gave a structured substrate alternating lines with or without **1**. MIMIC is a soft lithography technique allowing to build defined structure in micrometer scale by using a polymeric stamp as a template. We used a polydimethylsiloxane (PDMS) stamp to grow SAMs of different line width (between 15 and 50 µm).

Time-of-flight secondary ion mass spectrometry (TOF-SIMS) (Figure 2b and S4) and atomic force microscopy (AFM) (Figure S5) revealed the patterned structure onto solid substrates. There is a small different height between neighbouring lines (circa 0.2 nm), which is very close to the AFM instrument resolution. However, the difference between lines is better defined using chemical composition via TOF-SIMS. Although we didn't observed an ion fragment corresponding to the whole molecule, by TOF-SIMS we were able to plot the patterned substrate by identifying small organic ion fragments from **1** and inorganic fragments from the unfunctionalized surface. In addition, condensation experiments carried out on silicon substrate confirmed the formation of patterned SAMs (Figure S6).

The photophysical characterization of the homogenous SAM of **1** onto ITO substrate (Figure 1b) displays a behaviour similar to that in solution (Table S1). The absorption and excitation maxima are slightly blue shifted, while the hypsochromic shift in the emission in more evident, with maximum at 420 nm instead of 456 nm. Interestingly, the photophysical properties are affecting by the condition used to form the SAMs (Figure S7). By increasing the temperature up to 40 °C for 24 h, the absorption peak raises, indicating higher coverage of the surface. However, the emission slightly decreases, probably due to a self-quenching process. If the reaction time is reduced to 3 h at 40 °C, the monolayer shows a low intensity absorption band with maximum at 354 nm, indicating low coverage of the surface. Interestingly, in such conditions the PL

Figure 1. Absorption, excitation (PLE) and emission (PL) spectra of **1** (a) in DMF (2 µM) and (b) onto ITO surface.

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band appears broader with maximum at 500 nm and a shoulder around 425 nm. By comparing spectra arising from different SAM preparations, we can hypothesize that the formation of SAMs proceeds through different steps.[19] At low coverage, the molecules form aggregates characterized by a red shifted emission. By increasing the surface coverage, the dyes reorganize in ordered molecular SAM resulting in the increased emission at 420 nm and the disappearance of the band at 500 nm. Studies to determine the driving force of the sequential arrangement (dipole-dipole interaction, dispersion interactions or steric hindrance) are under investigation in our laboratories.

Although the QY in solid state is lower than in solution, we were able to observe the blue emission of the organic SAM also by fluorescence microscopy using a DAPI filter (Figure 2c and 2d). This clearly indicates the success of the strategy adopted to grow SAMs of spirobifluorene molecule.

The cyclic voltammetric analysis (see Table S2), carried out in DMF/0.1 M TBAP at 25 °C, also confirmed the absence of any sizeable effect of the linker on the redox properties of the spirobifluorene derivatives. The formal potential ($E°$) values were obtained as the average between the cathodic and anodic peak potentials. Compound **1** shows similar electrochemical behavior to a series of fluorene and spirobifluorene-based bifunctional organic dyes previously investigated by us[12a] (see, e.g., Figure S8). Two CV peaks are detected in the negative-going scan. The first peak (R1) shows a peak-to-peak separation ($\Delta E_{p,R1}$) compatible with the reversible formation of the fluorene radical anion. The second reduction peak (R2), attributed to the generation of dianion, is only partially reversible at low scan rates. Fully reversibility was however obtained at relatively higher scan rates, thus allowing its $E°_{R2}$ to be determined. The oxidation peak is fully reversible with a ΔE_p distinctly larger (Table S2) than the typical one-electron value of 59 mV at 25 °C.[20] It is also significantly larger than the ca. 29 mV separation expected for a fully developed two-electron process.[21] This behavior, as previously observed,[12a] is due to the fact that the two triphenylamine moieties are oxidized at very similar potentials, and the minor interaction between the two redox centers point to two poorly interacting HOMOs, therefore entropic reasons make the second process less favored by a factor ($2RT/F$) ln 2 = 35.6 mV (at 25 °C).[22]

Similar electrochemical behaviours were observed for the ITO modified with **1**. In this case, the surface confined CV was investigated at different scan rate in order to quantify the surface coverage of the SAM (see Figure S9). The experimental data provide a surface density of spirobifluorene groups (Γ_1) of 2.4×10^{-11} mol cm^{-2}, which is very similar to the values reported in literature for ITO surfaces bearing different functionalizations.[23]

The ECL properties of SAMs of **1** onto ITO substrate were investigated using the coreactant strategy. Differently from ECL annihilation, where the radicals involved in the excited state formation are electrochemically generated upon consecutive reduction and oxidation of the same chemical precursor, the use of a coreactant assures the generation of intermediates that, after oxidation or reduction, act as strong

reductant or oxidant agent. These species are capable of reacting with one of the electrogenerated radicals of the emitter producing an excited state.[1] Typically, coreactant ECL is used when one of the radical ion is not stable or its formation cannot be achieved before the background oxidation or reduction of the solvent, or the supporting electrolyte, or both. In our case, since the ECL emitter **1** is covalently linked onto the ITO substrate and its diffusion is prevented, the use of a coreactant is necessary to achieve ECL. The ECL emission intensity of the SAM **1** onto ITO substrate was investigated by cyclic voltammetry (CV) using benzoyl peroxide (BPO) as "reductive oxidation" coreactant (Figure 3), which follows the reaction mechanism schematized in scheme 1.[24] In particular, after reduction at the electrode surface (eq. 1), the BPO radical anion is converted to the strong oxidant species Ph-CO$_2^•$ (eq. 1), which subsequently reacts with the radical anion of the spirobifluorene (eq. 2), leading to the generation of the emitting excited state (eq. 3).

The ECL emission using BPO as coreactant reported in Figure 3a occurs in the potential region where the reduction of both coreactant and spirobifluorene is achieved. The ECL spectra recorded in the same experimental conditions (Figure 3b) presents a broad band with maximum at around 440 nm. Furthermore, our previous studies on this kind of spirobifluorene compounds suggest that the luminescence comes from a singlet excited state.[12a,14] It is worth noting the similarity between the ECL and the PL spectra recorded for SAMs grown at different temperature (Figure S7 and S10), which further supports our hypothesis about the stepwise formation of SAMs onto solid surface.

The ECL quantum yields was calculated, via a comparative method, relative to the conventional Ru(bpy)$_3^{2+}$, as the photons emitted per dye-molecule. In line with the very high ECL QY of analogues spirobifluorene luminophores measured in the homogeneous ECL,[14] the SAM of **1** shows 3 times higher ECL intensity compared with Ru(bpy)$_3^{2+}$ (see Figure S11 and SI for the details).

In summary, we reported the modification of ITO surface by SAMs of spirobifluorene-based dye either grown homogeneously or patterned by MIMIC. Together with a full characterization of the functionalized substrates, the investigation of ECL properties on pure organic dye in solid state are here reported for the first time. The data validate the self-assembly strategy, opening to novel opportunities in the field of electrochemiluminescent multicolour applications on solid state.
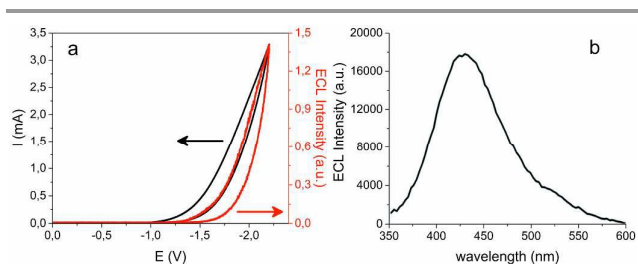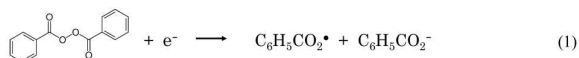

Figure 3. a) CV and ECL emission intensity and b) ECL emission spectra with BPO of SAM of **1** onto ITO substrate. Measurements performed in deaerated ACN

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with BPO 7 mM and TBAH 40 mM. a) CV recorded at scan rate: 0.1 V/s. PMT bias 750 V. Potentials reported vs Ag/AgCl 3 M. b) ECL emission spectra: voltage applied   -2.5 V vs Ag. Integration time: 1 s. Increment: 3 nm. PMT bias 750 V.

$$C_6H_5CO-O-OC-C_6H_5 + e^- \longrightarrow C_6H_5CO_2^\bullet + C_6H_5CO_2^- \qquad (1)$$

$$C_6H_5CO_2^\bullet + \text{—SPIRO-TPA}^{\bullet-} \longrightarrow \text{—SPIRO-TPA}^* + C_6H_5CO_2^- \qquad (2)$$

$$\text{—SPIRO-TPA}^* \longrightarrow \text{—SPIRO-TPA} + h\nu \qquad (3)$$

Scheme 1. Possible ECL reaction mechanism with coreactant onto electrode surface.

Notes and references

1 (*a*) *Electrogenerated Chemiluminescence*, ed. A. J. Bard, Marcel Dekker, New York, 2004; (*b*) Z. Liu, W. Qi and G. Xu, *Chem. Soc. Rev.*, 2015, **44**, 3117; (*c*) J. R. Forster, P. Bertoncello and Keyes E. Tia, *Annu. Rev. Anal. Chem.*, 2009, **2**, 359; (*d*) M. M. Richter, *Chem. Rev.*, 2004, **104**, 3003; (*e*) G. Valenti, A. Fiorani, H. Li, N. Sojic and F. Paolucci, *ChemElectroChem*, 2016, **3**, 1990.

2 (*a*) J. Y. Kim, S. Cheon, H. Lee, J.-Y. Oh, J.-I. Lee, H. Ryu, Y.-H. Kim and C.-S. Hwang, *J. Mater. Chem. C*, 2017, **5**, 4214; (*b*) T. Kasahara, S. Matsunami, T. Edura, R. Ishimatsu, J. Oshima, M. Tsuwaki. T. Imato, S. Shoji, C. Adachi and J. Mizuno, *Sens. Actuators A*, 2014, **214**, 225.

3 P. Bertoncello and P. Ugo, *ChemElectroChem*, 2017, **4**, 1663.

4 L. Xu, Z. Zhou, C. Zhang, Y. He and B. Su, *Chem. Commun.*, 2014, **50**, 9097.

5 (*a*) K. Kadimisetty, S. Malla, N. P. Sardesai, A. A. Joshi, R. C. Faria, N. H. Lee and J. F. Rusling, *Anal. Chem.*, 2015, **87**, 4472. (*b*) B. S. Munge, T. Stracensky, K. Gamez, D. Dibiase, and J. F. Rusling, *Electroanalysis*, 2016, **28**, 2644. (*c*) M. Sentic, F. Virgilio, A. Zanut, D. Manojlovic, S. Arbault, M. Tormen, N. Sojic, and P. Ugo, *Anal. Bioanal. Chem.*, 2016, **408**, 7085; (*d*) G. Valenti, M. Zangheri, S. E. Sansaloni, M. Mirasoli, A. Penicaud, A. Roda and F. Paolucci, *Chem. Eur. J.*, 2015, **21**, 12640.

6 G. Valenti, S. Scarabino, B. Goudeau, A. Lesch, M. Jovic, E. Villani, M. Sentic, S. Rapino, S. Arbault, F. Paolucci, and N. Sojic, *J. Am. Chem. Soc.*, 2017, **139**, 16830.

7 (*a*) W. Miao, *Chem. Rev.*, 2008, **108**, 2506 and references therein; (*b*) G. Valenti, E. Rampazzo, S. Bonacchi, L. Petrizza, M. Marcaccio, M. Montalti, L. Prodi and F. Paolucci, *J. Am. Chem. Soc.*, 2016, **138**, 15935; (*c*) H. C. Moon, T. P. Lodge and C. D. Frisbie, *J. Am. Chem. Soc.*, 2014, **136**, 3705; (*d*) Y. Kim and J. Kim, *Anal. Chem.*, 2014, **86**, 1654.

8 (*a*) C.-H. Yang, M. Mauro, F. Polo, S. Watanabe, I. Muenster, R. Fröhlich and L. De Cola, *Chem. Mater.*, 2012, **24**, 3684; (*b*) K. N. Swanick, M. Sandroni, Z. Ding and E. Zysman-Colman, *Chem. Eur. J.*, 2015, **21**, 7435; (*c*) L. Chen, E. H. Doeven, D. J. D. Wilson, E. Kerr, D. J. Hayne, C. F. Hogan, W. Yang, T. T. Pham and. P. S. Francis, *ChemElectroChem*, 2017, **4**, 1797; (*d*) S. Ramachandra, F. Polo, F. Edafe, K. C. Schuermann, C. A. Nijhuis, P. Belser, W. F. Reus, G. M. Whitesides and L. De Cola, *Pure Appl. Chem.*, 2011, **83**, 779; (*e*) E. H. Doeven, G. J. Barbante, E. Kerr, C. F. Hogan, J. A. Endler and P. S. Francis, *Anal. Chem.*, 2014, **86**, 2727; (*f*) E. Kerr, E. H. Doeven, G. J. Barbante, C. F. Hogan, D. J. Hayne, P. S. Donnelly and P. S. Francis, *Chem. Sci.*, 2016, **7**, 5271; (*g*) A. Kapturkiewicz, *ChemElectroChem*, 2017, **4**, 1604 and references therein.

9 M. Mydlak, C.-H. Yang, F. Polo, A. Galstyan, C. G. Daniliuc, M. Felicetti, J. Leonhardt, C. A. Strassert and L. De Cola, *Chem. Eur. J.*, 2015, **21**, 5161.

10 Q. Zhai, J. Li and E. Wang, *ChemElectroChem*, 2017, **4**, 1639 and references therein.

11 G. Valenti, E. Rampazzo, S. Bonacchi, T. Khajvand, R. Juris, M. Montalti, M. Marcaccio, F. Paolucci and L. Prodi, *Chem. Commun.*, 2012, **48**, 4187.

12 (*a*) F. Rizzo, F. Polo, G. Bottaro, S. Fantacci, S. Antonello, L. Armelao, S. Quici and F. Maran, *J. Am. Chem. Soc.*, 2017, **139**, 2060; (*b*) H. Li, J. Daniel, J.-B. Verlhac, M. Blanchard-Desce and N. Sojic, *Chem. Eur. J.*, 2016, **22**, 12702; (*c*) H. Qi, Y.-H. Chen, C.-H. Cheng and A. J. Bard, *J. Am. Chem. Soc.*, 2013, **135**, 9041; (*d*) H. Qi, C. Zhang, Z. Huang, L. Wang, W. Wang and A. J. Bard, *J. Am. Chem. Soc.*, 2016, **138**, 1947; (*e*) H. Li, A. Wallabregue, C. Adam, G. M. Labrador, J. Bosson, L. Bouffier, J. Lacour and N. Sojic, *J. Phys. Chem. C*, 2017, **121**, 785.

13 A. Venkatanarayanan, A. Martin, K. M. Molapo, E. I. Iwuoha, T. E. Keyes and R. J. Forster, *Electrochem. Commun.*, 2013, **31**, 116.

14 F. Polo, F. Rizzo, M. Veiga-Gutierrez, L. De Cola and S. Quici, *J. Am. Chem. Soc.*, 2012, **134**, 15402.

15 a) F. Schlüter, K. Riehemann, N. S. Kehr, S. Quici, C. G. Daniliuc and F. Rizzo, *Chem. Commun.*, 2018, **54**, 642; b) G. Bottaro, F. Rizzo, M. Cavazzini, L. Armelao and S. Quici, *Chem. Eur. J.*, 2014, **20**, 4598; c) T. Nakagawa, S.-Y. Ku, K.-T. Wong and C. Adachi, *Chem. Commun.*, 2012, **48**, 9580; d) T. P. I. Saragi, T. Spehr, A. Siebert, T. Fuhrmann-Lieker and J. Salbeck, *Chem. Rev.*, 2007, **107**, 1011.

16 (*a*) F. Cecchet, G. Fioravanti, M. Marcaccio, M. Margotti, L. Mattiello, F. Paolucci, S. Rapino and P. Rudolf, *J. Phys. Chem. B*, 2005, **109**, 18427; (*b*) J. Jalkh, S. Thiery, J.-F. Bergamini, P. Hapiot and C. Poriel, *J. Phys. Chem. C*, 2017, **121**, 14228.

17 A. Schweig, U. Weidner, D. Hellwinkel and W. Krapp, *Angew. Chem. Int. Ed.*, 1973, **12**, 310.

18 a) E. Kim, Y. Xia and G. M. Whitesides, *J. Am. Chem. Soc.*, 1996, **118**, 5722; b) B. Vonhören, M. Langer, D. Abt, C. Barner-Kowollik and B. J. Ravoo, *Langmiur*, 2015, **31**, 13625; c) M. Buhl, M. Staniford, S. Lamping, M. Körsgen, H. F. Arlinghaus, U. Kynast and B. J. Ravoo, *Langmuir*, 2017, **33**, 8799..

19 a) S. Onclin, B. J. Ravoo and D. N. Reinhoudt, *Angew. Chem. Int. Ed.*, 2005, **44**, 6282; b) D. K. Aswal, S. Lenfant, D. Guerin, J. V. Yakhmi and D. Vuillaume, *Anal. Chimica Acta*, 2006, **568**, 84.

20 R. S. Nicholson and I. Shain, *Anal. Chem.* 1964, **36**, 706.

21 D. S. Polcyn and I. Shain, *Anal. Chem.* 1966, **38**, 370.

22 F. Ammar and J.M. Saveant, *Electroanal. Chem.* 1973, **47**, 215.

23 K. M. Roth, A. A. Yasseri, Z. Liu, R. B. Dabke, V. Malinovskii, K.-H. Schweikart, L. Yu, H. Tiznado, F. Zaera, J. S. Lindsey, W. G. Kuhr and D. F. Bocian, *J. Am. Chem. Soc.*, 2003, **125**, 505.

24 (*a*) S. Antonello and F. Maran, *J. Am. Chem. Soc.*, 1999, **121**, 9668; (*b*) G. Valenti, C. Bruno, S. Rapino, A. Fiorani, E. A. Jackson, L. T. Scott, F. Paolucci and M. Marcaccio, *J. Phys. Chem. C*, 2010, **114**, 19467.

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