Supporting information section

*In-situ* fluorescence spectroscopy correlates ionomer degradation to reactive oxygen species generation in an operating fuel cell

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Evaluation of R6G in the presence of platinum

The fluorescence spectrum of R6G in the absence and presence of platinum are shown in Figure S1. It was observed that R6G retained its strong fluorescence signal after exposure to platinum (Pt) particles. A small drop in fluorescence signal upon addition of Pt ink was caused by the attenuation of fluorescence signal by the black colored Pt particles. A detailed discussion of these results is presented in the main manuscript.

Note: Fluorescence spectra were collected via ex-situ fluorescence experiments. Please see our previous work for a detailed description of the experiment.  

![Fluorescence Spectrum](image)

**Figure S1:** Fluorescence response of R6G upon addition of platinum catalyst ink. No changes in the fluorescence spectrum were observed upon the addition of platinum.
**Determination of R6G sensitivity to ROS**

The sensitivity of R6G to ROS was measured using an ex-situ fluorescence experiment using Fenton’s reagent (a mixture of ammonium iron (III) sulfate and hydrogen peroxide solution). Please see our previous work for a detailed description of the experiment. The results shown in Figure S2 confirmed that the photophysical properties of R6G were unaltered upon addition of Fenton’s reagent. A more detailed discussion of these results is presented in the main manuscript.

![Fluorescence response of R6G upon addition of Fenton’s reagent](image)

**Figure S2**: Fluorescence response of R6G upon addition of Fenton’s reagent (transition metal catalyst – iron (II) sulfate and hydrogen peroxide) to generate ROS. A small fluorescence decay was observed after addition of 200 µL of 3% H$_2$O$_2$. Subsequent addition of H$_2$O$_2$ showed no effect on the fluorescence intensity of R6G.

**Fluorescence resonance energy transfer (FRET) between R6G and 6CFL**

Figure S3 shows the fluorescence spectrum of 6CFL and the absorbance spectrum of R6G. R6G underwent fluorescence resonance energy transfer (FRET) with 6CFL when the dye-infused membranes were situated next to each other. Exciting 6CFL at 440 nm resulted in a fluorescence emission at 485 nm. This emitted signal was absorbed by R6G. The two resultant spectra, shown in Figure S3, overlap, demonstrating that FRET could occur between the two dye molecules. The excited R6G emits a fluorescence signal at 550 nm. The Förster radius, i.e. the distance where 50% of the electron energy transfer (fluorescence quenching) takes place between the donor (6CFL) and acceptor (R6G) dye molecules, was determined from the overlap spectra in Figure S3 in the SI section. The Förster radius was estimated to be between 30 Å to 50 Å. FRET therefore occurs at the interface between the Nafion®-R6G/Nafion®-6CFL membranes. In our previous work, we showed that the fluorescence beam emanating from the embedded optical fiber probe passes through the interface of the central Nafion®-6CFL membrane and the Nafion® barrier layer.
Therefore, the construction of the tri-layer membranes (Nafion®-R6G/Nafion®-6CFL/Nafion®-R6G) will facilitate the FRET phenomenon at the interface. Figure S4 in the SI sections shows the oscillating R6G fluorescence signal and a slight decay in the 6CFL fluorescence signal for the tri-layer membranes (Nafion®-R6G/Nafion®-6CFL/Nafion®-R6G) during In-situ fluorescence measurements. The oscillating behavior of the R6G was attributed to the FRET phenomenon and to the sensitivity of the fluorescence response of R6G to water content and pH.2-4

FRET can occur between 6CFL (donor) and R6G (acceptor) dye pairs since the fluorescence spectrum of 6CFL overlaps with the absorbance spectrum of R6G (Figure S3). The Förster radius for 6CFL-R6G dye pair was calculated using the procedure described by Roller et al.2 See equation (1) below. An acceptor extinction coefficient (\(\varepsilon(\sigma)\)) of 61400 dm³ mol⁻¹ cm⁻¹ for R6G in Nafion® was used in the calculation. Because the exact quantum yield of the donor dye was unknown, the quantum yield of donor (6CFL) was varied between 0.05 to 0.99 resulting in Förster radii (R₀) values between 30Å to 50 Å. Energy efficiency (equation (2)) was determined to be 99.99% assuming a distance of separation (R) between the two dyes of 1 nm. A critical distance of separation to avoid the FRET phenomenon was found vary between 4.8 nm to 7.9 nm. It is likely that the distance of separation between 6CFL and R6G at the interface falls within this range. The oscillatory behavior of R6G during In-situ fluorescence experiments (Figure S4) is attributed to FRET, as well as to contributions from variation in water content. R6G has been reported to be sensitive to water content and pH.3,2,4

\[
\text{Fluorescence of 6CFL} \\
\text{Absorbance of R6G}
\]

**Figure S3:** Normalized fluorescence spectrum of 6CFL overlapped with the normalized absorbance spectrum of R6G. The area underneath the overlap is used to determine the Förster radius. See equation 1.3
\[ R^o = \frac{9000 \eta(10 \cdot \kappa^2 \cdot \Phi_{EM} \cdot M_M)}{128 \pi^5 n^4 N} \int \frac{f(\nu) \cdot \varepsilon(\nu) d\nu}{\nu^3} \] 

- Integral overlap of fluorescence donor emission and acceptor absorbance. The expression was integrated with respect to the wave number using Simpson’s rule. Units for this solved integral are [M⁻¹ cm³]

\begin{align*}
N & \quad - \text{Avogadro’s number} \\
\varepsilon(\nu) & \quad - \text{Molar extinction coefficient of Acceptor dm}^3 \text{ mol}^{-1} \text{ cm}^{-1} \\
N & \quad - \text{Refractive index of solvent (water in this case) = 1.67 for this experiment} \\
\kappa & \quad - \text{Orientation factor of dye molecules (ranges between 0 and 4) = assumed to be 0.8167 (} \kappa^2 \text{ is often assumed to be 2/3).} \\
\Phi_{EM} & \quad - \text{Quantum yield of donor (ranges 0 to 1) – varied between 0.05 to 0.99} 
\end{align*}

The quantum yield of the donor dye (6CFL) was not available in the literature. Therefore, the quantum yield was varied between 0.05 to 0.99 resulting in a Förster radius of 30 Å to 50 Å.
Figure S4: Time series graphs of In-situ fluorescence response with the tri-layer membranes (Nafion®-R6G/Nafion®-6CFL/Nafion®-R6G) under N₂/N₂ at (i) 80°C, 50% RH and (ii) 80°C, 75% RH. The oscillating behavior of the R6G fluorescence signal and slight decay of 6CFL fluorescence signal was attributed to the FRET phenomenon and variations in water content.
**Figure S5:** Fluorescence spectra of trilayer membranes (Nafion®-R6G/Nafion®-6CFL/Nafion®-R6G) with R6G-Nafion® barrier membrane (showing FRET) and modified R6G-Nafion® barrier (no FRET).
Fuel cell performance of MEAs with and without fluorescent dyes but having the same membrane thickness

Figure S6 demonstrates that the performance of MEAs prepared with dye-infused Nafion® was comparable to the performance of MEAs prepared with Nafion® membranes without dye. However, both MEA configurations demonstrated a large ohmic resistance at high current densities, which was attributed to the thick membranes used (≈ 450 μm). We anticipated that the thick membranes could potentially cause an insufficient level of hydration inside the membrane, which could further exacerbate the issue of large ohmic resistances and lowering the gas crossover. To mitigate this effect adequate hydration of the PEM was ensured by passing humidified N₂/N₂ for the desired amount of time, as required to equilibrate the membrane at a particular relative humidity condition.

Because the in-situ studies need to accommodate an optical fiber probe (which is relatively thick), the thickness between the electrodes in the fuel cell with an imbedded fiber optic probe was around 450 μm. Therefore, to ascertain the effect of the dye on fuel cell performance, membranes of 450 μm were used to simulate the presence of the fiber optic probe. The consequence of this strategy is that the ohmic losses at high current densities will be large. But, the results presented in Figure S6 prove that the dye molecules do not significantly alter fuel cell performance. The ORR Tafel slopes in the low current density regime for both MEAs (with and without fluorescent dyes) were about the same (~56 mV/decade and ~63 mV/decade), respectively. These Tafel values are in-line with the values in the literature for ORR and also support the direct 4e- mechanism for ORR. Hence, it is established that ORR kinetics on the Pt/C electrodes remains unchanged in the presence/absence of 6CFL in the Nafion® membranes. Furthermore, the specific-area resistance and limiting current density for each MEA were about the same. Thus, the inclusion of the dye within the membrane do not significantly impact fuel cell performance.
**Figure S6:** Polarization curves obtained using MEAs used in the *in-situ* fluorescence experiments (Nafion®-R6G/Nafion®-6CFL/Nafion®-R6G) and FER measurements (multi-layered Nafion® membranes without dye, but of identical thickness) at 80 °C, 75% RH, under H₂/O₂ operation (2 stoich).
ORR activity of platinized electrodes in the presence of 6CFL in 0.1 M HClO₄

The dye-infused MEA fuel cell performance given in Figure S6 was subpar because a thicker membrane was used. Based on the results (Tafel slope, specific-area resistance) from Figure S6, we concluded that the dyes do not impact fuel cell performance. To further verify how the dyes may impact the ORR kinetics, estimation of ECSA (cyclic voltametry) and RDE experiments were performed with and without the presence of 6 CFL in the liquid electrolyte.

Estimation of  electrochemically active surface area (ECSA):

![Graph showing cyclic voltammograms for 0.1 M HClO₄ and 0.1 M HClO₄ + 800 µM 6CFL.]

**Figure S7:** Cyclic voltammograms obtained on a Pt/C (46%, TKK) catalyst surface and in N₂ saturated (i) 0.1 M HClO₄ solution (ii) 0.1 M HClO₄ + 800 µM 6CFL solution; sweep rate: 50 mV/s.

Figure S7 shows the cyclic voltammogram obtained on Pt/C in the two different electrolytes. ECSA was calculated from the H₂ desorption region of Figure S7 using equation 2.

\[
ECSA = \frac{q_{Pt}}{0.21[Pt]}
\]

(2)

Where, \( q_{Pt} \) is the charge for H₂ desorption (mC/cm²-geometric), 0.21 mC/cm²-Pt represents the charge due to one monolayer of H⁺ on Pt and \([Pt]\) is the platinum loading in the catalyst ink (mg Pt/cm²-geometric).

ECSA of Pt/C in 0.1 M HClO₄ and 0.1 M HClO₄ + 800 µM 6CFL are found to be 55 m²/gₚt and 49 m²/gₚt. A large decrease in ECSA was predicted in the presence of 6CFL since it was shown that 6CFL has a strong interaction with Pt (established in our previous work where the
fluorescence signal of 6CFL was compromised in the presence of platinum\(^1\). It should be noted that the 6CFL to platinum ratio in the cell setup is quite high and thus, there is more than enough 6CFL to cover the surface of platinum if 6CFL adsorption to platinum occurs. However, only a 10% reduction in ECSA occurred when 6CFL is present in the electrolyte solution. This result was contradictory to our prediction. Therefore, it is believed that 6CFL does not adsorb to the platinum surface. An alternative explanation to account for the 6CFL interaction with platinum that compromises 6CFL’s fluorescence signal may entail through space interaction between the platinum catalyst and dye or 6CFL forming a complex with platinum ions (which arrive from the dissolution of the platinum catalyst).

**Demonstration of ORR kinetics using RDE experiment:**

Figure S8 and S9 shows the polarization curves collected at different rotation rate on Pt/C for ORR in the 0.1M HClO\(_4\) and 0.1M HClO\(_4\) + 800 µM 6CFL electrolyte solutions respectively. From the data obtained at different rotation rates, the plot of \(i^{-1} vs. \omega^{-1/2}\) (Koutecky–Levich plot) were obtained. \(i = \) current density in mA/cm\(^2\) and \(\omega =\) rotation rate. Using Equation 3, kinetic current\((i_k)\) and number of electron transferred \((n)\) were estimated. See SI Figure S10 for K-L plots.

\[
\frac{1}{i} = \frac{1}{i_k} + \frac{1}{0.62 \cdot n \cdot F \cdot D^{1/2} \cdot \omega^{-1/2} \cdot \nu^{-1/6} \cdot c}
\]  

where, \(i\) - measured current density (mA/cm\(^2\)), \(i_k\) - kinetic current density (mA/cm\(^2\)), \(n\) - number of electrons transferred, \(F\) - Faraday constant, \(A\) - surface area of the electrode, \(D\) - diffusion coefficient of the oxygen in the electrolyte, \(\omega\) - rotation rate of the electrode, \(\nu\) - kinematic viscosity of the electrolyte, \(c\) - concentration of the ion in the bulk of the solution.

The \(i_k\) for Pt/C in 0.1M HClO\(_4\) and 0.1M HClO\(_4\) + 800 µM 6CFL electrolyte solutions at 0.650V vs SCE (0.906 V vs. NHE) were found to be 70 µA/cm\(^2\) and 60µA/cm\(^2\) respectively. The literature value for \(i_k\) on Pt/C was around 75 µA/cm\(^2\) which is in good agreement with the value reported here.\(^8,9\) The estimated number of electrons transferred during ORR for both electrolyte solutions was about 4, which is ideal for ORR kinetics. The kinetic current values and number of electrons transferred in presence of 0.1 M HClO\(_4\) + 800 µM 6CFL electrolyte solution are comparable to the electrolyte without 6CFL. A small decrease in the ORR kinetic parameters (also observed in the fuel cell performance experiment) are negligible. Based on these results, the minimal inclusion of 6CFL in the fuel cell will not impede the ORR kinetics.
**Figure S8**: Polarization curves obtained with a RDE for O$_2$ reduction on a Pt/C (46%, TKK) catalyst surfaces in 0.1 M HClO$_4$ solution at different rotation rates; sweep rate 5 mV/s.

**Figure S9**: Polarization curves obtained with a RDE for O$_2$ reduction on a Pt/C (46%, TKK) catalyst surfaces in 0.1 M HClO$_4$ + 800 µM 6CFL solution at different rotation rates; sweep rate 5 mV/s.
**Figure S10:** Koutecky–Levich plot of ORR data of Pt/C(46%, TKK) in 0.1 M HClO₄ and 0.1 M HClO₄ + 800 µM 6CFL electrolyte solution.

**References**


