Electrochemiluminescent Cells Based on Zeolite-Encapsulated Host–Guest Systems: Encapsulated Ruthenium Tris-bipyridyl

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Abstract: An electrochemiluminescent cell has been developed that has an active layer consisting of ruthenium tris-bipyridyl encapsulated inside zeolite Y supercages. Operation of the cell requires the addition of polyethylene glycol as the solid electrolyte. The cell, which exhibits electrical conductivity behavior typical of a semiconductor, has an optimum operating voltage of 3 V. Ion exchange of sodium by cesium and vapor deposition of calcium metal inside the zeolite pores enhance the electrochemiluminescent efficiency of the cell by a factor of 4.

Keywords: electrochemiluminescent cell · host–guest systems · luminescence · ruthenium · zeolites

Introduction

Zeolites are among the preferred hosts in supramolecular systems.[1,2] Remarkable effects in the control of the *intrinsic* molecular properties of the guest have frequently been observed.[3,4] Perhaps one of the most general phenomena observed upon incorporation inside the zeolite micropores is an increase in the stability of the embedded organic molecule.[3,5,6] This stabilization arises in most cases from the confinement and immobilization of the guest in a restricted space and from the effective protection exerted by the rigid zeolite framework against the attack of atmospheric and other external reagents.[4,7]

In spite of the promise of supramolecular host–guest systems based on zeolites in photonics, electronics, and other applications in nanotechnology,[8–13] examples of real applications of zeolites in these fields have not yet been brought to fruition. This is in contrast to the situation in areas such as catalysis, gas purification, water softening and heavy metal ion removal, solvent drying, etc. where zeolites are commercialized in multi-ton amounts.[2,14,15]

One possibility that would be worthwhile exploring is the development of light-emitting devices based on zeolite host–guest systems. The use of a zeolite-based supramolecular host–guest system in the emitting layer of a light-emitting device could be a viable strategy to stabilize the emitting guest and also increase the operation life of light-emitting device based on organic compounds and metallic complexes.

The development of such zeolite-based light-emitting devices is challenging because charge transport between the external electrodes and the internal guests in the zeolite has to be demonstrated, and the construction of submicrometric films of zeolite particles encapsulating an electroluminescent guest is not an easy task.

In the present work, we describe how zeolite-based systems containing an occluded guest can be used for the development of light-emitting electrochemical cells (LEEC). Specifically, our report deals with the electroluminescent activity of ruthenium tris-bipyridyl encapsulated in alkali metal ion exchanged Y-faujasites.

Results and Discussion

Our work is based on the well-known property of the ruthenium tris-bipyridyl complex to act as an orange-emitting electrochemiluminescent complex.[16–23] On the other hand, there are also many precedents in the literature showing that ruthenium tris-bipyridyl can be encapsulated inside zeolite Y supercages by means of a ship-in-a-bottle synthesis.[24–40] The synthetic procedure, originally developed by Lundsford et al.,[40] was later improved by Dutta and Turberville.[36,37] This method consists of introducing $[Ru(NH_3)_6]^{3+}$ from an aqueous solution by ion exchange, subsequent com-

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plexation in the solid state with 2,2′-bipyridine, and a final series of exhaustive solid–liquid extractions. Scheme 1 summarizes the preparation of [Ru(bpy)$_3$]@NaY used in this
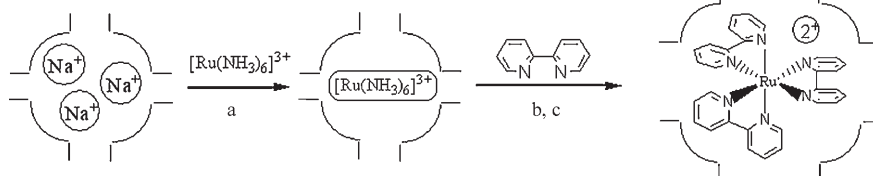
Scheme 1. *Ship-in-a-bottle* synthesis of the ruthenium tris-bipyridyl complex encapsulated inside zeolite Y. a) Ion exchange at 60 °C, 7 h. b) Thermal treatment at 200 °C, 24 h. c) Exhaustive solid–liquid extraction.

work. The resulting [Ru(bpy)$_3$]@NaY (average of 0.11 complexes per supercage) was suspended in an aqueous NaCl solution to ion exchange and remove the externally located [Ru(bpy)$_3$]$^{2+}$ to ensure that no complexes are located on the external particle surface. It has been reported that high complex loading (up to 0.5 complex per supercage) can be detrimental for the purity of the encapsulated material.[41] From the initial [Ru(bpy)$_3$]@NaY, a sample containing the same [Ru(bpy)$_3$]$^{2+}$ loading but with Cs$^+$ as the accompanying cation was obtained by ion exchange with Cs(OAc).

Considerable prior evidence on zeolite-encapsulated [Ru-(bpy)$_3$]$^{2+}$ has demonstrated that this complex occupies internal cavities in the zeolite particle.[32, 34, 36, 37] In our case, the internal location of [Ru(bpy)$_3$]$^{2+}$ was confirmed by: i) XPS analysis of the external zeolite surface and observation of the absence of Ru atoms, and ii) inefficient partial oxygen quenching (less than 10 % reduction of the intensity) of [Ru-(bpy)$_3$]$^{2+}$ phosphorescence. In solutions, oxygen strongly quenches the [Ru(bpy)$_3$]$^{2+}$ emission, while the impeded oxygen diffusion inside the zeolite pores effectively protects encapsulated [Ru(bpy)$_3$]$^{2+}$ triplets against quenching. Thus, observation of minor oxygen quenching provides simple indirect evidence of the presence of [Ru(bpy)$_3$]$^{2+}$ inside the pores.

In view of the activity of [Ru(bpy)$_3$]$^{2+}$ for the preparation of LEECs and its easy zeolite encapsulation, we have investigated the possibility of generating electrochemiluminescence from [Ru(bpy)$_3$]@zeolite. To demonstrate the feasibility of this original concept for LEECs, we have prepared a cell consisting of a [Ru(bpy)$_3$]@NaY layer located between a transparent conductive indium tin oxide (ITO) anode and an aluminum counterelectrode (Figure 1).
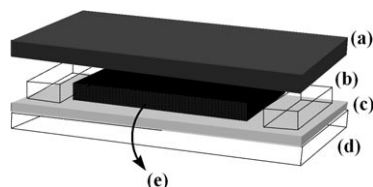

Figure 1. Parts of an electroluminescent cell based on [Ru(bpy)$_3$]@NaY as the electroluminescent component. a) aluminum, b) adhesive tape, c) ITO, d) glass, e) [Ru(bpy)$_3$]@NaY.

The electrical conductivity of these cells shows an intensity versus voltage (*I–V*) profile that is typical of a semiconductor, with a 20-fold increase in the electrical conductivity beyond a breaking voltage of 5.1 V direct current (dc) (Figure 2).[42] Blank controls without any zeolite layer or a amorphous silica-based cell prepared analogously (plot IV, Figure 2) demonstrate that this *I–V* plot does represent the electrical conductivity of our [Ru(bpy)$_3$]@NaY sample.[42]
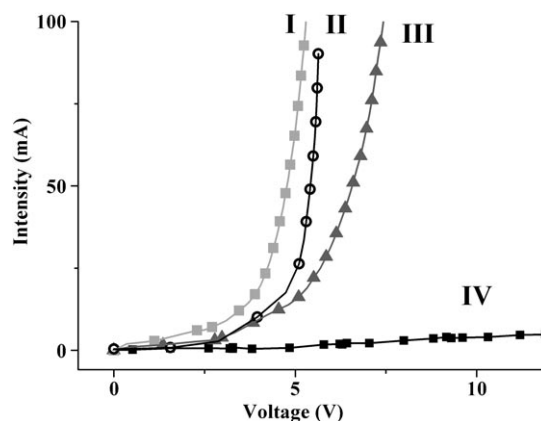

Figure 2. *I–V* plots measured for I) CsY, II) NaY, III) [Ru(bpy)$_3$]@NaY, and IV) SiO$_2$.

Comparison of the electrical conductivity of [Ru(bpy)$_3$]@NaY with that of unloaded NaY (plot II, Figure 2) shows that the latter has higher conductivity and lower breaking voltage. These *I–V* profiles in zeolites have been attributed to ionic conductivity: the internal charge-balancing cations migrate in a sufficiently high electrical field. This ion migration is similar in [Ru(bpy)$_3$]@NaY and NaY; however, when the ruthenium complex is adsorbed inside the cavities, this imposes some restrictions on the Na$^+$ mobility that explains the somewhat higher conductivity of NaY. CsY also exhibits a lower breaking voltage than NaY, and this fact will become relevant latter when we address the influence of the accompanying alkali cation on the electrochemiluminescence of encapsulated [Ru(bpy)$_3$]$^{2+}$.

A series of cells containing [Ru(bpy)$_3$]@NaY were tested for electrochemiluminescence on connecting them to constant dc voltages between 0 and 10 V. No emission from dry cells was observed.

It is a common situation in electroluminescent cells that the presence of hole-injection or electron-injection compounds considerably improves the performance of the cell by promoting charge transport from the electrodes into the active layer.[43–46] In addition, in our case, the LEEC cell may require relocation of charge-balancing cations with the creation of a gradient with different alkali metal ion concen-

trations (higher close to the cathode and lower close to the anode) in the zeolite film. Because in the device shown in Figure 1, the electroluminescent film is constituted by independent zeolite particles without electrical connectivity among them, probably requiring interparticle ion and charge (electron and hole) transport, we added polyethylene glycol (PEG, average molecular weight 6000 dalton) to the [Ru(bpy)$_3$]@NaY layer. It is envisioned that PEG will occupy only the outer space between the zeolite particles without entering the micropores, thus promoting percolative (outside the zeolite particles) ionic and hole conductivity through the film. Under these circumstances and in the presence of PEG, we were able to observe orange electrochemiluminescence from the [Ru(bpy)$_3$]@NaY cell. Apparently, PEG is acting as a solid polyelectrolyte and thus plays a crucial role in the interparticle charge transport from the working electrodes through the zeolite layer. This charge transport is necessary for the LEEC to operate. It is known that PEG forms complexes with alkali metal ions with a structure similar to crown ethers.[47] Migration of the alkali ions is facilitated by a complexation-decomplexation-jump-complexation mechanism. Moreover, PEG is a hole-transport polymer: the lone pairs of the oxygen atoms intervene in this migration. Scheme 2 illustrates two possible charge-
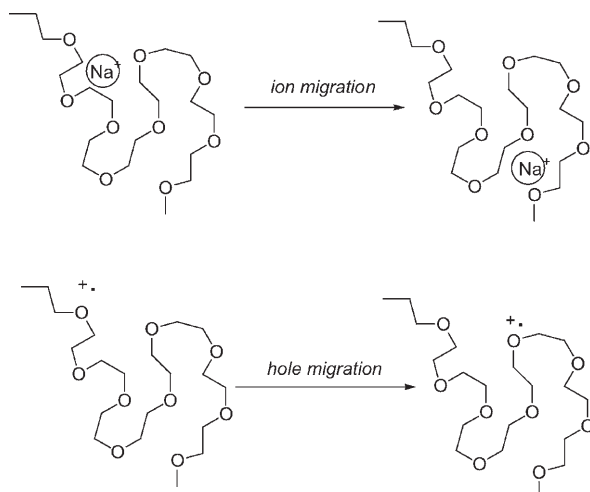
Scheme 2. Two possible mechanisms for interparticle charge transport promoted by PEG.

transport mechanisms promoted by PEG. This interpretation agrees with the widespread use of PEG to permit ion migration in silica as well as silicates.[48–50] To support this assumption, we tested other electrolytes as alternatives to PEG, namely poly(acrylamide-co-2-hydroxyethyl acrylate) and 1-butyl-4-methylimidazolium hexafluorophosphate, which also exhibit the same ability to activate the electrochemiluminescence of the zeolite-encapsulated [Ru(bpy)$_3$]$^{2+}$ complex.

Figure 3 shows the electrochemiluminescence spectrum of the [Ru(bpy)$_3$]@NaY cell, which coincides with the photoluminescence spectrum of [Ru(bpy)$_3$]@NaY (inset of Figure 3). This coincidence proves that the lowest [Ru-
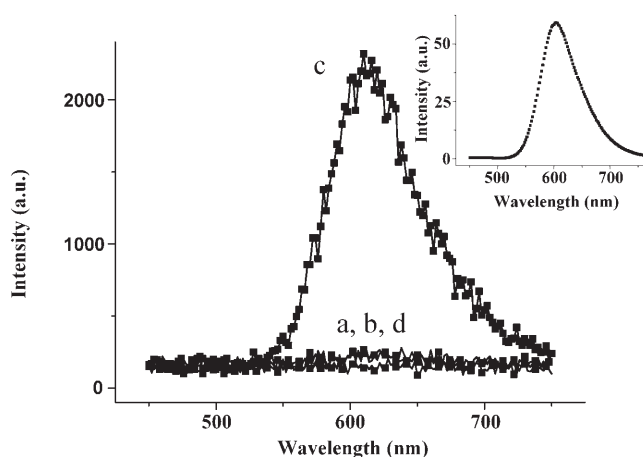

Figure 3. Intensity of the emitted light versus wavelength plot for [Ru-(bpy)$_3$]@NaY electroluminescent cell. Several voltages were applied to the sample: a) 1 V, b) 2.4 V, c) 3 V, and d) 4 V. Inset: Photoluminescence spectrum of [Ru(bpy)$_3$]@NaY.

(bpy)$_3$]@NaY triplet excited state is the ultimate species being generated in the cell and is thus responsible for the light emission. The optimum voltage was 3 V; lower or higher voltages led to a decrease in the emission intensity.

It is very likely that the electrochemiluminescence mechanism of [Ru(bpy)$_3$]$^{2+}$ encapsulated in zeolites is analogous to the mechanism proposed for pure [Ru(bpy)$_3$]$^{2+}$ films, which is based on the electrochemical oxidation of [Ru(bpy)$_3$]$^{2+}$ to [Ru(bpy)$_3$]$^{3+}$ near the anode and the electrochemical reduction of [Ru(bpy)$_3$]$^{2+}$ to [Ru(bpy)$_3$]$^{+}$ near the cathode.[21–23] The triplet excited state is generated in the intermediate region as consequence of the collapse of [Ru(bpy)$_3$]$^{2+}$ and [Ru(bpy)$_3$]$^{2+}$ (Scheme 3).

The temporal profile of the light emission was followed by monitoring (at 3 V dc) the emission at $\lambda_{max=}$610 nm, and was in agreement with the previous mechanistic proposal. The initial intensity built up rapidly until a stationary regime with a steady constant intensity was achieved at times longer than 45 min (Figure 4). Switching the applied
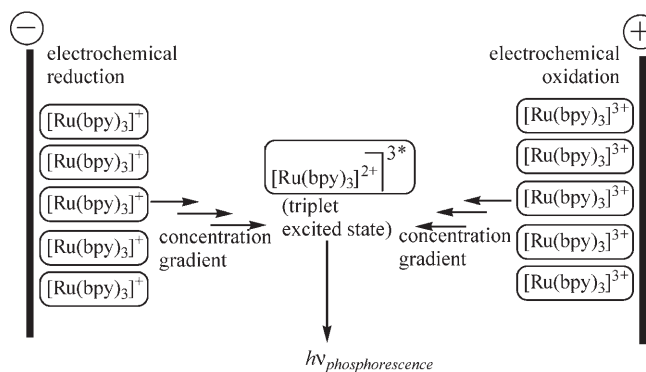
Scheme 3. Mechanistic proposal for the electrochemiluminescence emission of [Ru(bpy)$_3$]@NaY. A steady-state gradient of reduced and oxidized ruthenium complex is generated in the vicinity of the electrodes. Collapse of [Ru(bpy)$_3$]$^{+}$ and [Ru(bpy)$_3$]$^{3+}$ gives rise to the emissive triplet excited state.

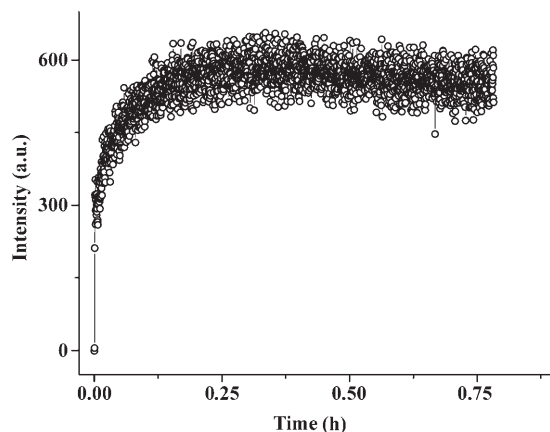Figure 4. Emitted light intensity monitored at $\lambda_{max} = 610$ nm versus time for a [Ru(bpy)$_3$]@NaY electroluminescent cell.

Figure 5. Emitted light intensity versus wavelength for a [Ru(bpy)$_3$]@CsY electrochemiluminescent cell. Voltages applied to the sample: a) 0 V, b) 3 V without calcium deposition and c) 3 V after calcium deposition and equilibration for 24 h. Inset: Emitted light intensity versus wavelength for a [Ru(bpy)$_3$]@zeolite electroluminescent cell: a) [Ru(bpy)$_3$]@CsY at 0 V, b) [Ru(bpy)$_3$]@CsY at 3 V, and d) [Ru(bpy)$_3$]@NaY at 3 V.

voltage off and on led to the prompt disappearance and re-appearance of the electroluminescent emission with the same intensity as it was before the voltage was switched off. The initial increase is well documented in LEECs based on [Ru(bpy)$_3$]$^{2+}$ and has been explained as indicating the generation throughout the cell of a stationary distribution of species with the formation of a gradient of [Ru(bpy)$_3$]$^{3+}$ concentration decaying from the anode and another [Ru(bpy)$_3$]$^{+}$ concentration in the cathode.[21–23] By analogy with the electrochemiluminescence mechanism in pure [Ru(bpy)$_3$]$^{2+}$ films, we propose that the same redox processes are occurring inside the zeolite micropores with the electrochemical generation of [Ru(bpy)$_3$]$^{3+}$ and [Ru(bpy)$_3$]$^{+}$ or holes and electrons as reported. In this regard, it is worth noting that the electrochemical response of zeolite-encapsulated guests is well documented and has been the subject of numerous studies aimed at developing catalysts, sensors, charge storage devices, etc.[51–55] In particular, the electrochemical oxidation/reduction of zeolite-encapsulated [Ru(bpy)$_3$]$^{2+}$ has been reported some time ago.[56,57]

Because electrochemiluminescence requires electron transport in and out of the zeolite interior where [Ru(bpy)$_3$]$^{2+}$ is located, we anticipated that by changing the nature of the zeolite charge balancing cation, it should be possible to modify the electrochemiluminescence efficiency of the cell. In fact, the cell efficiency was increased two-fold from one sample of the [Ru(bpy)$_3$]@NaY (loading 0.11 complexes per supercage) to another twin sample derived from it in which Cs^{+} instead of Na^{+} was the charge balancing cation [Ru(bpy)$_3$]@CsY (see Figure 5) with an estimated luminance of 0.4 cd × m^2 and an electrical efficiency of 2.5 lumen × W^{-1}. Because it is well known in zeolite chemistry that charge-balancing cations occupy intracrystalline positions,[1,2] the fact that the electrochemiluminescence intensity of CsY is higher than that of NaY, together with the internal location of [Ru(bpy)$_3$]$^{2+}$, are evidence supporting the hypothesis that electrochemiluminescence in zeolites is essentially an intracrystalline phenomenon.
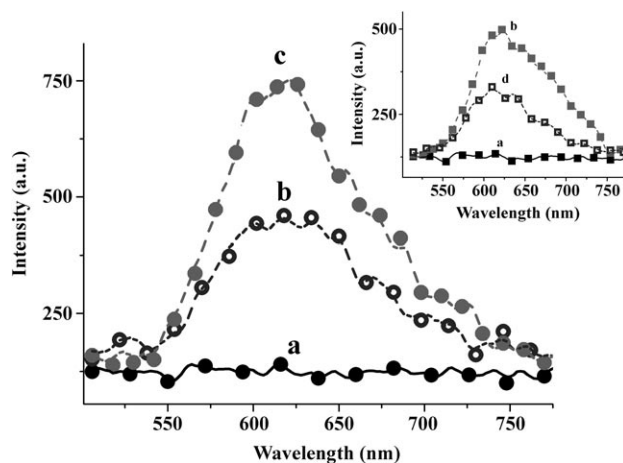
Following the same strategy of adding additives that can enhance charge transport inside the zeolite particles, we proceeded to perform vapor deposition of calcium metal inside the zeolite samples containing ruthenium tris-bipyridyl. Deposition of metal films is a common procedure to enhance the efficiency of electroluminescent cells by promoting electron injection into the active emitting layer.

In this context, it is interesting to mention that there are reports of zeolite Y incorporating alkali and alkaline earth metals inside the cavities.[58–60] In these cases, the clusters of strongly reducing metals become ionized to afford metal cations and as well as electrons that flow quite freely inside the zeolite pores (electrides).[58] While vapor deposition of calcium on glass produces a metallic mirror surface that becomes immediately oxidized upon exposure to the atmosphere, such a mirror was not observed when calcium was deposited on [Ru(bpy)$_3$]@NaY and [Ru(bpy)$_3$]@CsY, which suggests that the sublimed calcium atoms have been adsorbed in the zeolite pores. One extra advantage of using zeolites is that in the process of calcium deposition, the high temperature of the sublimed metal atoms can negatively affect the cell efficiency by partially degrading the active layer. This negative thermal effect is minimized by heat dissipation through the zeolite framework that has a high heat capacity.

The beneficial influence of calcium absorption on the operation of LEEC is manifested by a significant increase in the electrochemiluminescence efficiency. Thus, Figure 5 shows that calcium deposition in [Ru(bpy)$_3$]@CsY doubles the electrochemiluminescence emission intensity. The behavior is also observed for [Ru(bpy)$_3$]@NaY, for which a similar electrochemiluminescence enhancement upon calcium adsorption occurs. This effect of calcium deposition is even more remarkable considering that the zeolite was handled in the atmosphere and that the measurements were car-

ried out 24 h after sample equilibration in the atmosphere. Thus, it is also clear that the zeolite framework is protecting co-adsorbed calcium metal from immediate attack of moisture and CO_2 that would occur in submicrometric calcium films if they were exposed to the atmosphere. In other words, in spite of the high reactivity of calcium, it is not absolutely necessary to work under an inert atmosphere when calcium is adsorbed inside the zeolite pores.

Conclusion

Considering that zeolites are among the preferred porous host materials,[10,61–65] the observed electrochemiluminescence in a zeolite-encapsulated guest may open a new direction in the application of zeolites outside the field of catalysis. Indeed, in the same way as zeolites can dramatically stabilize highly unstable species, they could serve as a rigid matrix to increase the operation life of LEDs, which would eventually allow their manufacture and operation under more amenable conditions. In this sense, the easy handling of ruthenium encapsulated in zeolites containing calcium metal constitutes a remarkable example of the advantages of our methodology. Further work is underway to optimize and increase the efficiency of this type of electroluminescent cells to fully exploit their promising potential.

Experimental Section

Preparation of [Ru(bpy)₃]@NaY: NaY, [Ru(NH₃)₆]³⁺, and 2,2′-bipyridyl were commercial samples. NaY (5 g) was added to a solution of [Ru-(NH₃)₆]³⁺ (150 mg) in distilled water (50 mL), and the suspension was stirred for 7 h at 60 °C. The solid was filtered and washed exhaustively with distilled water. The resulting pink powder was dried in the atmosphere, and then mixed with 2,2′-bipyridine (l2.5 g). The mechanical mixture was pelletized by pressing (5 atm, 1 min), crushing the wafers, and sieving. The pellets were heated (200 °C, 24 h) under flowing nitrogen and exhaustively extracted with water and ethanol. Ion exchange from [Ru(bpy)₃]@NaY to [Ru(bpy)₃]@CsY was achieved by stirring a suspension of [Ru(bpy)₃]@NaY (1 g) in an aqueous solution of CsAcO (10 mL, 1 M) at 80 °C for 5 h. The solid was filtered and washed several times with distilled water. The resulting partially exchanged orange solid was submitted to two consecutive ion-exchange treatments as described above. Finally, the resulting powder was calcined (300 °C, 5 h) in the open atmosphere.

Preparation of electroluminescent cells: Before preparation of the cell, indium tin oxide (ITO) glass was cleaned by ultrasonic irradiation in an acetone bath for 5 h, and the aluminum counterelectrode was polished. A 1×1 cm² area was defined on the ITO glass by means of adhesive tape. A suspension of zeolite in ethanol was deposited and spread with a razor blade on the ITO surface. After evaporation of ethanol in the open atmosphere, the adhesive tape was replaced by a clean one. This new tape prevents short-circuiting between the aluminum and ITO electrodes. This gave a homogeneous 1×1 cm² zeolite film about 50-μm thick. Following this, a drop of 1% aqueous solution of polyethylene glycol was added over the zeolite layer as an active electrolyte. Finally, the aluminum counterelectrode was placed on top of the wet zeolite film, and the cell was held together by two clamps.

Measurements of electrical conductivity: A voltage ramp was generated with an acquisition card; the voltage was then converted to current with a voltage-to-current converter that was applied to the cell. A current

sweep was made for each pair of V–I values. A four-wire system was used to measure the voltage/current thus avoiding errors produced by the wire resistances. This four-wire setup uses two wires for current injection and the remaining two for measuring the voltage on the cell. A calibrated resistor with a 0.1% tolerance was used to calibrate the electronic system.

Measurements of electrochemiluminescence: The cell electrodes were connected to a DC potentiostat and several values of constant voltage between 0 and 10 V were applied. The emission of the electroluminescent material was monitored between 300 and 800 nm by placing the cell inside the sample chamber of a modified PTI 814 spectrofluorimeter. The emission spectrum acquired by applying a constant voltage of 0 V was used as a blank measurement. The lifetime of the cells was measured by monitoring the emission of the sample at 610 nm with a constant voltage of 3 V versus time.

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