



Ceric ammonium nitrate (CAN) as oxidizing or nitrating reagent for organic reactions in ionic liquids

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ABSTRACT

The reaction of ceric ammonium nitrate, $(\text{NH}_4)_2[\text{Ce}(\text{NO}_3)_6]$ or CAN, with naphthalene and 2-methylnaphthalene in the ionic liquid 1-ethyl-3-methylimidazolium triflate showed that the reaction products are strongly dependent on the water content of the ionic liquid and that cerium(IV) in the ionic liquid can electrochemically be regenerated.

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Ammonium hexanitratocerate(IV) is without doubt the most important cerium(IV) reagent for organic synthesis.^{1–7} This compound is known to most organic chemists as ceric ammonium nitrate, or as CAN for short. The formula $(\text{NH}_4)_2[\text{Ce}(\text{NO}_3)_6]$ reflects that the cerium(IV) ion is surrounded by six nitrate groups and that the ammonium ions are counter ions to compensate for the negative charge of the hexanitratocerate(IV) coordinating unit. CAN is a one-electron oxidation reagent. Typical examples are the oxidation of benzyl alcohol to benzaldehyde,⁸ of toluene to benzaldehyde,⁹ of naphthalene to 1,4-naphthoquinone,¹⁰ and of 1,4-hydroquinones to the corresponding 1,4-quinones.^{11,12} CAN can also be used as nitrating agent,^{13,14} initiator for radical polymerization reactions,¹⁵ or reagent to remove protecting groups.^{16,17} Cerium(IV) reagents are relatively mild oxidation reagents in comparison with other metal-based oxidation reagents such as potassium permanganate or chromium(VI) salts. Moreover, cerium(IV) salts are much less toxic than chromium(VI) salts. Because cerium(IV) salts are one-electron oxidizing agents and because they have a relatively high molecular mass, large quantities of cerium(IV) salts are required for stoichiometric reactions. Therefore, indirect and catalytic reactions have been developed.^{18–21} Of special interest is cerium-mediated electro-synthesis, where the redox active cerium(IV) species are electrochemically regenerated.^{22–25} The main advantage of CAN over other cerium(IV) reagents is its higher solubility in organic solvents, but the reagent suffers sometimes from unwanted side reactions. Different solvents can be selected for reactions with ammonium hexanitratocerate(IV) as reagent. The most popular solvents are (in decreasing order of importance) water, acetonitrile, dichloromethane, THF and methanol.⁶ Often mixtures of these solvents are used. Other solvents have found only marginal use for this type of reactions. It should be mentioned that in many reac-

tions in apolar solvents, CAN is used as a suspension; thus under heterogeneous reaction conditions.

Although ionic liquids have been used as an alternative solvent for a plethora of organic reactions,^{26–31} only very few studies of cerium(IV)-mediated reactions in ionic liquids have been described.³² Bar et al. have studied CAN-mediated oxidative free radical reaction in the ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate.³³ Mehdi et al. screened different cerium(IV) salts and imidazolium ionic liquids for oxidation reactions.³⁴ They found that ceric ammonium nitrate and cerium(IV) triflate are the most suitable cerium(IV) salts and that 1-alkyl-3-methylimidazolium triflates are the preferred ionic liquids. In present Letter, the reaction of CAN with naphthalene and 2-methylnaphthalene in the ionic liquid 1-ethyl-3-methylimidazolium triflate, $[\text{C}_2\text{mim}][\text{OTf}]$ is described. The purpose of this study was to show how the chemoselectivity of CAN-mediated reactions can be altered by changing the water content of the ionic liquid. Moreover, we give a proof-of-principle for the electrochemical regeneration of cerium(IV) in the ionic liquid.

The ionic liquid selected for this work was 1-ethyl-3-methylimidazolium triflate, which will be abbreviated throughout this study as $[\text{C}_2\text{mim}][\text{TfO}]$ (Fig. 1). The selection was based on the fact that previous screening of imidazolium ionic liquids in our laboratory has revealed that ceric ammonium nitrate is well soluble in this ionic liquid.³⁴ $[\text{C}_2\text{mim}][\text{TfO}]$ is a hydrophilic ionic liquid and is in all ratios miscible with water. $[\text{C}_2\text{mim}][\text{TfO}]$ is a room temperature ionic liquid (melting point = -9°C) and its viscosity is 45 cP at 25°C .³⁵ As the organic substrates, naphthalene and 2-methylnaphthalene were selected. It is known that cerium(IV) salts can

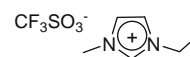


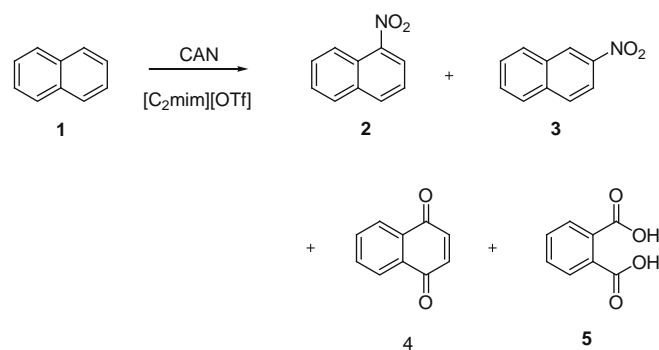
Figure 1. Structure of the ionic liquid 1-ethyl-3-methylimidazolium triflate, $[\text{C}_2\text{mim}][\text{TfO}]$.

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oxidize naphthalene to 1,4-naphthoquinone in aqueous solvents.^{36,10} Nitration of naphthalene derivatives by CAN has been reported for CAN suspended in dichloromethane in the presence of 2 equiv of sulfuric acid,³⁷ and for CAN dissolved in acetonitrile.¹⁴ The oxidation product of 2-methylnaphthalene is 2-methyl-1,4-naphthoquinone, which is better known as menadione or vitamin K₃. It is being used as a supplement for the vitamins K₁ and K₂ in animal feed and it is also a synthetic intermediate of vitamin K. Vitamin K₃ is produced on an industrial scale by oxidation of 2-methylnaphthalene with stoichiometric amounts of chromium(VI) oxide in sulfuric acid.³⁸ Other procedures to obtain menadione use catalytic amounts of metal derivatives in combination with strong oxidizing agents such as hydrogen peroxide and periodic acid.^{39,40} Non-catalytic oxidation of 2-methylnaphthalene has also been reported, but such procedures require potent mixtures of strong acids. Earlier work has shown that cerium(IV) salts can also oxidize 2-methylnaphthalene to 2-methyl-1,4-naphthoquinone.²²

In Table 1, the experiments involving the reaction between CAN and naphthalene in [C₂mim][TfO] are summarized.⁴¹ In dry ionic liquid, nitration is the predominant reaction. The nitration of naphthalene results in the formation of two isomers: 2-nitronaphthalene and 1-nitronaphthalene, with 1-nitronaphthalene being the major component. Notice that for nitration of naphthalene, a 1:1 molar ratio CAN: naphthalene is sufficient. Although at higher CAN:naphthalene ratios (up to 6:1) the conversion of naphthalene is higher, the amount of side products increases. These side products are 1,4-naphthoquinone and phthalic acid (identified by GC–MS) (Scheme 1). The formation of 1,4-naphthoquinone and phthalic acid requires an oxygen source. However, the oxygen atoms are provided by the traces of water left in the ionic liquids. It was found that the hydrophilic ionic liquid [C₂mim][OTf] is very difficult to dry. Initially, the ionic liquid contained 0.05 mass% of water (determined by Karl Fischer titration). After drying the ionic liquid at 80 °C under vacuum or freeze-drying it for several hours, still 0.03 mass % was present in the ionic liquid. Consequently, we were not able to make this hydrophilic ionic liquid completely anhydrous by our drying procedures. This explains why we always noticed trace amounts of oxidation products under conditions where complete nitration was expected. However, the amount of side products could be reduced by increasing the reaction temperature. While still 7% of oxidation products (1,4-naphthoquinone and phthalic acid) was observed for the nitration reaction of naphthalene at 100 °C, only 2% of oxidation products was detected when performing the same reaction at 150 °C or 180 °C. It is very likely that the high yield for the nitration reaction at elevated temperatures is due to the fact that the ionic liquid has a very low water content at these temperatures, so that the nitration reaction (no



Scheme 1. Reaction of CAN with naphthalene (1) in the ionic liquid [C₂mim][OTf], leading to the formation of 1-nitronaphthalene (2), 2-nitronaphthalene (3), 1,4-naphthoquinone (4) and phthalic acid (5).

water required) can efficiently compete with the oxidation reaction (water required).

In addition, complete conversion was already obtained after 1 h using the higher reaction temperatures. This clearly illustrates the advantage of performing reactions in ionic liquids at elevated temperatures.

In order to obtain a reasonable yield of 1,4-naphthoquinone, water has to be added to the ionic liquid. Moreover, oxidation of naphthalene into 1,4-naphthoquinone requires 6 equiv of cerium(IV) salt, because cerium(IV) is a one-electron oxidant, whereas nitration can be accomplished with only 1 equiv of CAN as the nitrating agent. More than the theoretically necessary amount of water (2 equiv) is beneficial for the formation of 1,4-naphthoquinone, but the reaction in pure water is not very selective toward the formation of 1,4-naphthoquinone. The addition of ionic liquid to pure water increases the solubility of naphthalene and consequently the oxidation proceeds smoother. The CAN-mediated reaction of naphthalene was also performed with compressed air as the oxygen source. When air was bubbled through the reaction mixture, complete conversion was obtained, but 78% of the naphthalene was nitrated while only 11% of 1,4-naphthoquinone and 11% of phthalic acid were formed. Hence, the oxidation of naphthalene toward 1,4-naphthoquinone proceeds better in the presence of water. The highest amount of 1,4-naphthoquinone was obtained after short reaction times. The longer the reaction proceeded, the more competition with nitration was observed. It should be noted that in none of the experiments 1,4-naphthoquinone could be obtained in a high yield. There was always a competition with nitration when CAN was used as the oxidizing agent.

Table 1
Reactions of CAN with naphthalene in the ionic liquid [C₂mim][OTf]^a

Entry	CAN (equiv)	amount of H ₂ O added (mL)	Time (min)	Temperature (°C)	Conversion (%)	Product distribution (%) ^c			
						1-Nitro	2-Nitro	NQ	PA
1	1	0	180	100	88	89	7	2	2
2	1	0	60	100	52	86	7	4	3
3	1	0	60	150	>98	90	8	1	1
4	1	0	60	180	>98	90	8	0	2
5	1	1	60	100	7	16	0	84	0
6	6	1	60	100	>98	62	5	32	1
7	6	0	30	100	>98	79	4	6	11
8	6	1	30	100	96	46	3	50	1
9	6	5	30	100	68	21	1	78	0
10	6	5 ^b	30	100	79	45	3	39	13

^a 1 mmol of naphthalene in 5 g of [C₂mim][OTf].

^b without ionic liquid, naphthalene does not dissolve in water.

^c 1-nitro: 1-nitronaphthalene; 2-nitro: 2-nitronaphthalene; NQ: 1,4-naphthoquinone; PA: phthalic acid.

Separation of the reaction products from the ionic liquid solvent after reaction was not easy. We found that extraction with toluene was the best option.

In the CAN-mediated reactions of 2-methylnaphthalene in $[\text{C}_2\text{mim}][\text{OTf}]$ only 2-methyl-1,4-naphthoquinone was observed as the oxidation product, and no oxidation of the methyl group was observed. Moreover, depending on the reaction conditions, various nitrated 2-methylnaphthalenes were obtained. Among these isomers, 1-nitro-2-methylnaphthalene was always formed as the major product (Scheme 2). This is in agreement with various other nitration procedures of 2-methylnaphthalene using nitric acid, wherein 2-methyl-1-nitronaphthalene is formed in the largest quantity (50–60%) among the six occurring nitrated isomers. The other isomers were formed in the following order: 7-methyl-1-nitro > 3-methyl-1-nitro > 6-methyl-1-nitro > 2-methyl-6-nitro > 2-methyl-3-nitro (in trace amounts). The experiments involving 2-methylnaphthalene are summarized in Table 2. Figure 2 gives an overview of the different isomers.

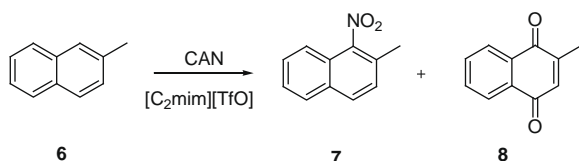
In order to obtain oxidation of naphthalene and 2-methylnaphthalene in the absence of the competing nitration reactions, reactions were also performed with hydrated cerium(IV) triflate, $\text{Ce}(\text{OTf})_4 \cdot x\text{H}_2\text{O}$, instead of CAN. Six equivalents of $\text{Ce}(\text{OTf})_4 \cdot x\text{H}_2\text{O}$ are required for the oxidation of naphthalene. However, such large amounts of $\text{Ce}(\text{OTf})_4 \cdot x\text{H}_2\text{O}$ could not be dissolved in $[\text{C}_2\text{mim}][\text{OTf}]$. Therefore, reactions were performed with 1 equiv of $\text{Ce}(\text{OTf})_4 \cdot x\text{H}_2\text{O}$ in order to check if some amount of 1,4-naphthoquinone could be obtained. However, the reaction of naphthalene in 5 g of $[\text{C}_2\text{mim}][\text{OTf}]$ and 1 mL of water in the presence of 1 equiv of $\text{Ce}(\text{OTf})_4 \cdot x\text{H}_2\text{O}$ did not proceed at 80 °C. At this temperature, naphthalene was poorly soluble in the water/ $[\text{C}_2\text{mim}][\text{OTf}]$ mixture. Higher reaction temperatures led however to sublimation of naphthalene out of the reaction mixture.

Because the reactions presented in this study require stoichiometric amounts of CAN and because CAN has a relatively high molecular mass ($M_r = 548.26$), large quantities of CAN are required. Therefore, a method to regenerate cerium(IV) in the ionic liquid solution would be highly desirable. A very promising route, which takes advantage of the electrochemical stability and the electric conductivity of ionic liquids is the electrochemical regeneration of cerium(IV). In the past, the electrochemical oxidation of cerium(III) to cerium(IV) in aqueous solutions of triflic acid or methanesulfonic acid has been studied. We investigated the possibility of

regenerating cerium(IV) in the ionic liquid phase which remained after extraction of the reaction products with toluene.

The initial electrochemical studies consisted of cyclic voltammetry measurements on the pure ionic liquid $[\text{C}_2\text{mim}][\text{OTf}]$ and on a solution of CAN in the ionic liquid.⁴² The electrochemical window of the ionic liquid was approximately 4 V, which is in agreement with literature data.⁴³ Cyclic voltammograms of solutions of 0.1 M, 0.2 M and 0.3 M of CAN in $[\text{C}_2\text{mim}][\text{OTf}]$ were measured and compared with the pure ionic liquid (see Fig. 3). The peak currents for the oxidation and reduction processes increase linearly with concentration up to 0.2 M. The peak current in the cyclic voltammogram labeled 0.3 M is not three times the value of the cyclic voltammogram with 0.1 M due to incomplete dissolution of CAN. In order to have more detailed information on the position of the oxidation and reduction peaks, experiments were performed using a reference electrode based on the ferrocene redox couple Fc/Fc^+ in $[\text{C}_2\text{mim}][\text{OTf}]$. With this reference electrode, the cyclic voltammogram of solutions of CAN in $[\text{C}_2\text{mim}][\text{OTf}]$ were measured. As can be seen in Figure 3, the reduction of cerium(IV) to cerium(III) occurs at about 0.8 V (or at 1.2 V vs SHE) and oxidation occurs at about 1.0 V (or at 1.4 V vs SHE). However, after oxidation of cerium(III) to cerium(IV) the electric current did not drop back to zero. Further experiments with the controlled addition of small amounts of water to the ionic liquid have indicated that this remaining electric current originates from the decomposition of traces of water in the ionic liquid. Additional experiments also showed that under the conditions at which cerium(III) is oxidized to cerium(IV), the ammonium group of $(\text{NH}_4)_2[\text{Ce}(\text{NO}_3)_6]$ is electrochemically stable.

The cyclic voltammetry study of CAN in $[\text{C}_2\text{mim}][\text{OTf}]$ indicated that it should be possible to reoxidize cerium(III) to cerium(IV) directly in the ionic liquid $[\text{C}_2\text{mim}][\text{OTf}]$. Hence, the ionic liquid phase obtained after the CAN-mediated oxidation reaction of benzyl alcohol to benzaldehyde was investigated for reoxidation of the cerium salt and reuse for further oxidation reactions. We have selected oxidation of benzyl alcohol rather than the oxidation of naphthalene as a model reaction for the electrochemical regeneration of cerium(IV), because the oxidation of benzyl alcohol by CAN is less prone to side reactions like nitrations. A mixture of 1 equiv of benzyl alcohol and 2 equiv of CAN in $[\text{C}_2\text{mim}][\text{OTf}]$ was heated and stirred in an oil bath at 100 °C during 6 h under nitrogen atmosphere. Afterwards, the solution was extracted with toluene and the organic phase was analyzed with gas chromatography using dodecane as the internal standard. A nearly quantitative conversion of benzyl alcohol was observed, with benzaldehyde as the main reaction product (95%), besides traces of benzyl alcohol and benzoic acid. Consequently, most of the cerium in the ionic liquid phase is after the reaction present under the form of cerium(III). The cerium-containing ionic liquid phase was heated under reduced pressure to remove traces of toluene. The resulting solution was introduced in the anode compartment of a two-compartment electrochemical cell. The cathode compartment was filled with pure ionic liquid. The oxidation of cerium(III) was performed



Scheme 2. Reaction of CAN with 2-methylnaphthalene (**6**) in the ionic liquid $[\text{C}_2\text{mim}][\text{OTf}]$, leading to the formation of 1-nitro-2-methylnaphthalene (**7**) and 2-methyl-1,4-naphthoquinone (**8**).

Table 2
Reactions of CAN with 2-methylnaphthalene in the ionic liquid $[\text{C}_2\text{mim}][\text{OTf}]^a$

Entry	CAN (equiv)	H_2O added (mL)	Time (min)	Conversion (%)	Product distribution (%) ^b				
					NQ	1-Nitro	8-Nitro	4-Nitro	5-Nitro
11	1	0	60	>98	14	40	19	17	10
12	6	1	300	>98	53	34	7	4	2
13	6	1	60	>98	54	30	8	5	3

^a 1 mmol of 2-methylnaphthalene in 5 g of $[\text{C}_2\text{mim}][\text{OTf}]$, oil bath adjusted to 100 °C.

^b NQ = 2-methyl-1,4-naphthoquinone; 1-nitro = 2-methyl-1-nitronaphthalene; 8-nitro = 7-methyl-1-nitronaphthalene; 4-nitro = 3-methyl-1-nitronaphthalene; 5-nitro = 6-methyl-1-nitronaphthalene.

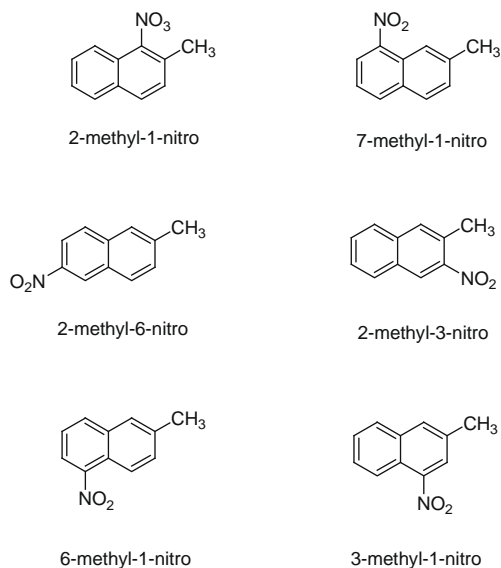


Figure 2. Different isomers formed upon nitration of 2-methylnaphthalene.

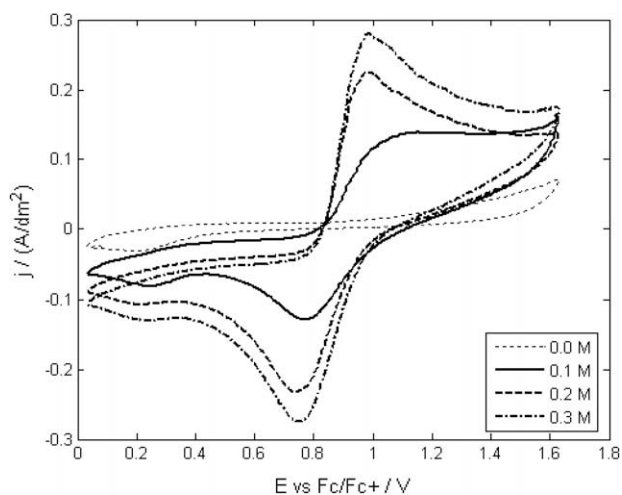


Figure 3. Cyclic voltammogram of solutions of CAN in $[C_2mim][OTf]$ at three different concentrations, measured at room temperature using a platinum working electrode and a Fc/Fc^+ reference electrode. The cyclic voltammogram of the ionic liquid $[C_2mim][OTf]$ is included for comparison.

potentiostatically, at a constant potential of 1.28 V versus Fc/Fc^+ (1.68 V vs SHE). The color of the solution changed from pale yellow to yellow-orange, which indicated that cerium(III) was at least partially oxidized to cerium(IV). The resulting cerium(IV)-containing ionic liquid was tested for oxidation of benzyl alcohol. During the subsequent reaction with benzyl alcohol, the solution turned yellow after a short time. After 6 h, the reaction mixture was extracted with toluene and the organic phase was analyzed with gas chromatography using dodecane as the internal standard. In this second run, 72% of benzyl alcohol was oxidized to benzaldehyde. Furthermore, the final ionic liquid phase was pale yellow to colorless. These experiments indicate that cerium(III) that is obtained after the oxidation reaction was partially reoxidized to cerium(IV) directly in the ionic liquid, which makes it possible to reuse this ionic liquid mixture for subsequent oxidation reactions. However, the conversion of benzyl alcohol to benzaldehyde was less than in the first experiment because some cerium was lost from the ionic liquid by diffusion from the anode to the cathode compartment.

The study of the reactions of naphthalene and 2-methylnaphthalene with ceric ammonium nitrate (CAN) in the ionic liquid 1-ethyl-3-methylimidazolium triflate shows that the outcome of the reaction strongly depends on the water content of the ionic liquid. Nitration is observed in dry ionic liquids, whereas an appreciable amount of oxidation products is formed in wet ionic liquids. However, nitration cannot be avoided, whatever the water content is. High yields of 1-nitronaphthalene and 2-nitronaphthalene (isomer ratio 90:8) could be obtained by performing the reaction between naphthalene and CAN at elevated temperatures (150–180 °C). This illustrates once again that ionic liquids are a good solvent for organic reactions at elevated temperatures, thanks to the very low vapor pressure and the thermal stability of these solvents.³⁴ The chemoselectivity of reactions in ionic liquids can thus be changed not only by a proper choice of the anion,⁴⁴ but also by modifying the water content. This Letter gives the proof-of-principle that the cerium in the ionic liquid can be electrochemically oxidized after reaction to the tetravalent state and the regenerated cerium(IV)-containing ionic liquid solutions can be reused for oxidation reactions. The system is still prone to improvement, because part of the cerium is lost during the electrolysis by diffusion to the cathode compartment. Further research is focused on the development of cerium-mediated electro-synthesis in ionic liquids.

Acknowledgments

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41. To a solution of CAN (6 mmol, 3.288 g) in 1-ethyl-3-methylimidazolium triflate, [C₂mim][OTf] (5 g, 3.6 mL) was added naphthalene (1 mmol, 128 mg) or 2-methylnaphthalene (1 mmol, 142 mg) and eventually some water (1 mL or 5 mL). At room temperature 6 mmol of CAN was not completely dissolved in 5 g of [C₂mim][OTf], but a clear solution was obtained upon heating. The mixture was stirred and heated in an oil bath adjusted to 100 °C. After a given period of time the solution was cooled and extracted with toluene (5 × 5 mL). The organic phase was dried with MgSO₄, which also removed traces of ionic liquid that would contaminate the injection system and/or the column of the gas chromatograph. The resulting sample was diluted with acetone and analyzed by gas chromatography. Similar experiments were performed with a CAN:substrate ratio of 1:1 instead of the above mentioned 6:1 ratio. In this case the amount of CAN used was 1 mmol (548 mg), with the other experimental conditions left unchanged.
42. The electrochemical experiments were conducted using a Solartron SI 1287 Electrochemical Interface. Cyclic voltammetry experiments were performed at a scan rate of 50 mV/s. The regeneration of cerium(IV) by oxidation of cerium(III) was performed potentiostatically. The working electrodes consisted of platinum wire (diameter: 0.5 mm, Goodfellow, 99.99%) sealed in epoxy resin. Before use, the working electrodes were mechanically polished with diamond paste (3 μm), rinsed in demineralized water, and dried. All potentials were measured versus a reference electrode based on a solution of ferrocene (Fc) and Fc⁺PF₆⁻ in [C₂mim][OTf] and are reported versus Fc/Fc⁺, whose standard reduction potential is +400 mV versus SHE.¹ The counter electrode was made of platinum. The electrochemical experiments were performed at room temperature in a two-compartment cell: both compartments were separated by a glass frit with pore sizes in the range 10–20 μm. The working electrode used during this experiment had a surface area of 0.196 mm².
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