RSC Advances

PAPER

View Article Online
View Journal | View Issue

Cite this: *RSC Adv.*, 2015, **5**, 32933

Synthesis of 1,2,4,5-tetrasubstituted imidazoles using 2,6-dimethylpyridinium trinitromethanide {[2,6-DMPyH]C(NO_2)$_3$} as a novel nanostructured molten salt and green catalyst†

Mohammad Ali Zolfigol,*[a] Saeed Baghery,[a] Ahmad Reza Moosavi-Zare*[b] and Seyed Mohammad Vahdat[c]

Received 20th February 2015
Accepted 24th March 2015

DOI: 10.1039/c5ra03241e

www.rsc.org/advances

2,6-Dimethylpyridinium trinitromethanide {[2,6-DMPyH]C(NO_2)$_3$}, as a novel nanostructured molten salt, efficiently catalyzed the synthesis of 1,2,4,5-tetrasubstituted imidazole derivatives by a one-pot four-component condensation reaction of benzil/benzoin, aldehydes, amine derivatives and ammonium acetate at room temperature under solvent-free conditions. Some advantages of the presented method are effective catalysis, excellent cost effectiveness and reusability of the catalyst. {[2,6-DMPyH]C(NO_2)$_3$} was fully characterized by IR, ^{1}H NMR, ^{13}C NMR and mass spectroscopy, X-ray diffraction patterns (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), thermogravimetry (TG) and derivative thermogravimetry (DTG) analyses.

Introduction

Multi-component reactions have been developed as an effective and influential tool in modern synthetic organic chemistry, facilitating the facile creation of several new bonds in one-pot reactions. Imidazole was first synthesized by Debus in 1858.[1] Compounds with the imidazole ring system have many pharmacological properties and play important roles in many biochemical procedures.[2] There are numerous methods available for the preparation of highly substituted imidazole derivatives, such as synthesis *via* a hetero-Cope rearrangement,[3] cyclization of sulfonamides with mesoionic 1,3-oxazolium-5-olates,[4] four-component condensation of arylglyoxals, primary amines, carboxylic acids and isocyanides on Wang resin,[5] condensation of 1,2-diones, aldehydes, primary amines and ammonia[6] and reaction of *N*-(2-oxo)-amides with ammonium trifluoroacetate.[7] Furthermore, they have attracted considerable attention because of their fungicidal,[8] antiinflammatory,[2] analgesic,[9] herbicidal[10] and anti-thrombotic activities.[11]

Room-temperature molten salts (RTMSs), correspondingly termed as room-temperature ionic liquids, are immiscible or only partially miscible with water (W); moreover, they have been explored to be favorable alternatives to conventional organic solvents and several new features have been observed in RTMS–W two-phase systems.[12–18] Molten salts have a significant potential as electrolyte materials. The molten salts, lately termed as "ionic liquids", have attracted considerable attention in numerous scientific fields.[12] Molten salts are convenient materials for transforming solid salts into liquids; moreover, significant efforts have also been made to polymerize molten salts into solid films. Various experiments have been carried out to develop an excellent ion-conductive matrix, and in this regard the polymerization of molten salts is a promising method to make highly ion-conductive polymer films.[19,20] In addition, methane reforming and methanol steam reforming are some applications of molten salts.[21,22]

It is well-understood that there is an increasing importance for more environmentally friendly methods in chemical synthesis, pharmaceutical industries and heterocyclic synthesis. This advanced development, termed as 'Green Chemistry' or 'Sustainable Technology', requires a paradigm change from traditional notions of process efficiency, which concentrate mainly on the yield of product, to one that allocates economic value, which concentrates on eliminating waste and the use of toxic and dangerous substances.[23a]

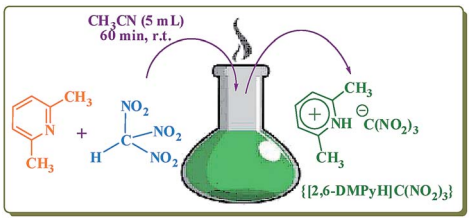
Solvent-free reactions, as one of the key green chemistry protocols, have been demonstrated to be an efficient technique for various organic transformations without using harmful organic solvents. Easier work up, decrease in reaction times and increase in yields are some other potential advantages of using solvent-free conditions.[23b,c]

[a]*Faculty of Chemistry, Bu-Ali Sina University, Hamedan 6517838683, Iran. E-mail: zolfi@basu.ac.ir; mzolfigol@yahoo.com; moosavizare@yahoo.com; Fax: +98 8138257407*

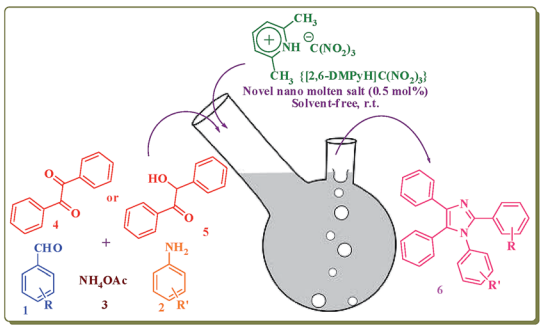
[b]*Department of Chemistry, University of Sayyed Jamaleddin Asadabadi, Asadabad 6541835583, Iran*

[c]*Department of Chemistry, Ayatollah Amoli Branch, Islamic Azad University, P.O. Box 678, Amol, Iran*

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c5ra03241e



Scheme 1 The synthesis of 2,6-dimethylpyridinium trinitromethanide {[2,6-DMPyH]C(NO_2)$_3$} as a nanostructured molten salt catalyst.



Scheme 2 The synthesis of 1,2,4,5-tetrasubstituted imidazole derivatives in the presence of {[2,6-DMPyH]C(NO_2)$_3$} as a novel nanostructured molten salt.

Life, which utilizes the most complex form of organic compounds on earth, needs the building of chemical bonds in an aqueous environment. Subsequently, nature's main use of water as a multipurpose solvent for organic and green chemistry should be considered as an example.[24]

In this work, we have designed a novel molten salt and catalyst, namely, 2,6-dimethylpyridinium trinitromethanide {[2,6-DMPyH]C(NO_2)$_3$} (Scheme 1), and employed it in a green, environmentally benign and effective method for the one-pot four-component synthesis of 1,2,4,5-tetrasubstituted imidazole derivatives from the reactions of benzil/benzoin, aldehydes, amine derivatives and ammonium acetate under solvent-free conditions at room temperature (Scheme 2).

Results and discussion

Characterization of 2,6-dimethylpyridinium trinitromethanide {[2,6-DMPyH]C(NO_2)$_3$} as a nanostructured molten salt catalyst

The structure of 2,6-dimethylpyridinium trinitromethanide {[2,6-DMPyH]C(NO_2)$_3$} as a novel nanostructured molten salt catalyst was studied and identified by FT-IR, ^{1}H NMR, ^{13}C NMR, mass, TG, DTG, XRD, SEM and TEM analyses.

The IR spectrum of the nanostructured molten salt showed a broad peak at 3437 cm^{-1}, which corresponds to the N–H stretching group on the pyridinium ring. Moreover, two peaks detected at 1634 cm^{-1} and 1384 cm^{-1} were related to the vibrational modes of NO_2 bonds (Fig. 1).

Furthermore, the ^{1}H NMR and ^{13}C NMR spectra of 2,6-dimethylpyridinium trinitromethanide {[2,6-DMPyH]C(NO_2)$_3$}

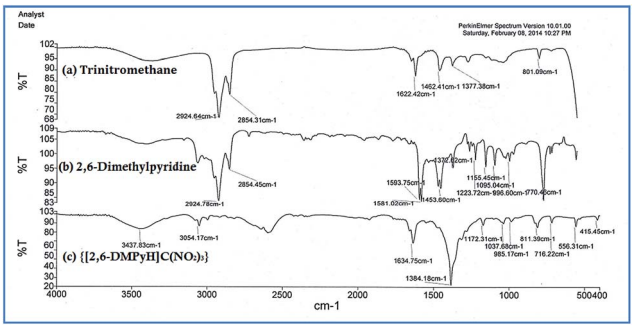


Fig. 1 The IR spectrum of trinitromethane (a); 2,6-dimethylpyridine (b); 2,6-dimethylpyridinium trinitromethanide {[2,6-DMPyH]C(NO_2)$_3$} (c).

in DMSO-d_6 are depicted in Fig. 2 and 3. The peak of the acidic hydrogen (N–H) in the nanostructured molten salt catalyst confirmed that the peak detected at 9.55 ppm in the ^{1}H NMR spectra for {[2,6-DMPyH]C(NO_2)$_3$} can be correlated to the hydrogen of the N–H functionalized 2,6-dimethylpyridinium salt (Fig. 2).

The ^{13}C NMR spectra of {[2,6-DMPyH]C(NO_2)$_3$} provided another evidence to confirm its structure. The peak presented at 70.25 can be related to the carbon of –C(NO_2)$_3$ group in trinitromethanide (Fig. 3).

The thermal gravimetric analysis (TGA) of [2,6-DMPyH]-C(NO_2)$_3$ was also carried out. The related diagrams are displayed in Fig. S3 and S4.† The thermal gravimetry (TG) and differential thermal gravimetric (DTG) analyses showed that the nanostructured molten salt catalyst was very stable and there was no evident mass loss before 190 °C. The significant weight loss occurred in the range of 190–500 °C, which can be attributed to the loss of [2,6-DMPyH]C(NO_2)$_3$.

Nanostructure of {[2,6-DMPyH]C(NO_2)$_3$} as a molten salt catalyst was studied by X-ray diffractometry (XRD) pattern (Fig. 4), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) (Fig. 5). In an attempt to confirm

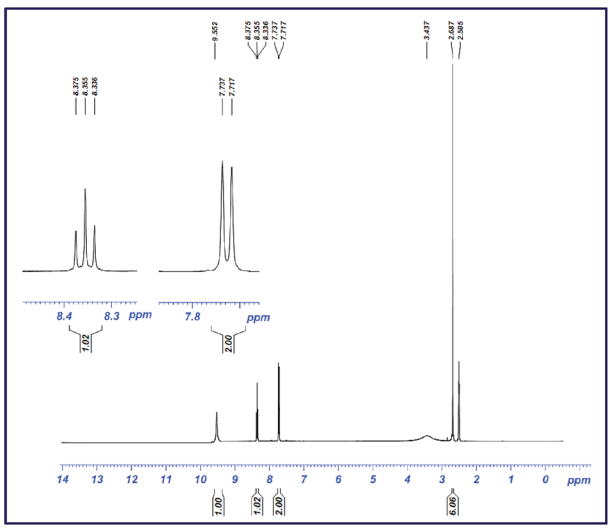


Fig. 2 The ^{1}H NMR spectrum of the {[2,6-DMPyH]C(NO_2)$_3$} as a novel nanostructured molten salt catalyst.

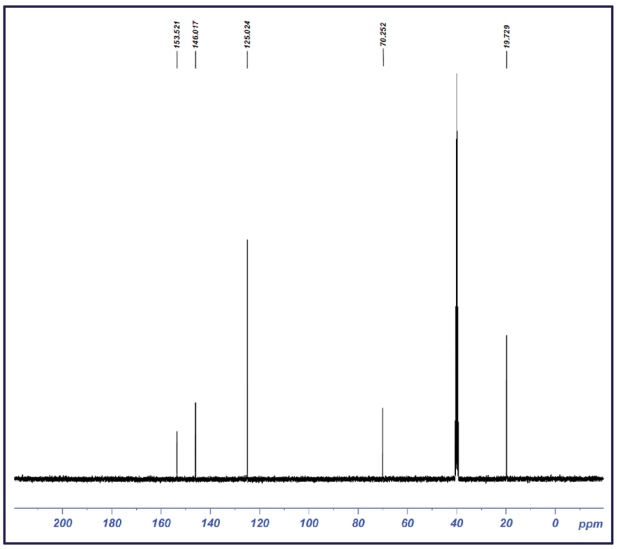


Fig. 3 The ^{13}C NMR spectrum of the {[2,6-DMPyH]C$(NO_2)_3$} as a novel nanostructured molten salt catalyst.

that {[2,6-DMPyH]C$(NO_2)_3$} was suitably synthesized, its XRD pattern was recorded. As presented in Fig. 4, the XRD patterns of the nanostructured molten salt catalyst reveal peaks at $2\theta \approx$ 12.10°, 13.30°, 16.00°, 20.40°, 20.80°, 22.90°, 24.30°, 25.60°, 26.30°, 26.70°, 28.00° and 34.00°, which were correspondingly confirmed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) (Fig. 5). The peak width (FWHM), size and inter-planar distance linked to the XRD pattern of {[2,6-DMPyH]C$(NO_2)_3$} were considered in the 2θ range from 12.10° to 34.00°, and the results obtained are summarized in Table 1. Average crystallite size D was considered using the Debye–Scherrer formula: $D = K\lambda/(\beta \cos \theta)$, where K is the Scherrer constant, λ is the X-ray wavelength, β is the half-maximum peak width, and θ is the Bragg diffraction angle. Consequently, the average size of the nanostructured molten salt catalyst attained from the abovementioned equation, was found to be in the range of 16.86–36.72 nm, which is fundamentally in accordance with the results obtained by scanning electron microscopy and transmission electron microscopy (Fig. 5).

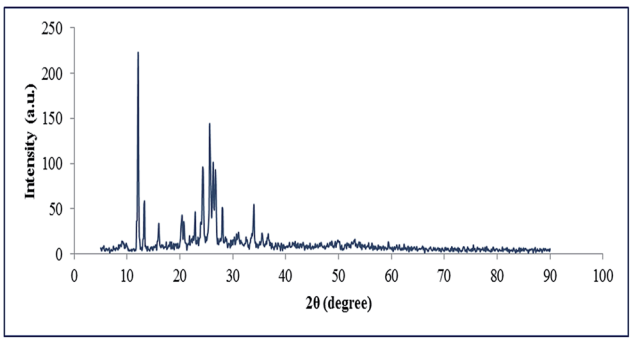


Fig. 4 The X-ray diffraction (XRD) pattern for the nanostructured molten salt catalyst.

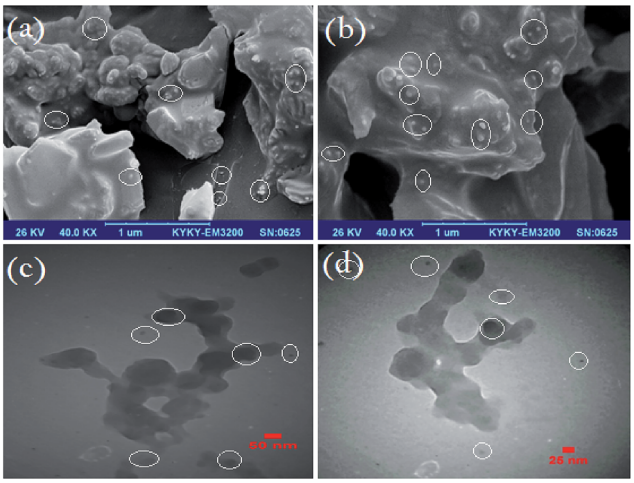


Fig. 5 Scanning electron microscopy (SEM) (a and b) and transmission electron microscopy (TEM) (c and d) of {[2,6-DMPyH]C$(NO_2)_3$} as a nanostructured molten salt catalyst.

Table 1 The X-ray diffraction (XRD) data for the nanostructured molten salt catalyst

Entry	2θ	Peak width [FWHM] (degree)	Size [nm]	Inter-planar distance [nm]
1	12.10	0.22	36.68	0.730578
2	13.30	0.22	36.72	0.664917
3	16.00	0.29	16.86	0.553268
4	20.40	0.41	19.83	0.434819
5	20.80	0.26	31.31	0.426548
6	22.90	0.23	35.35	0.387884
7	24.30	0.35	23.24	0.365844
8	25.60	0.25	32.30	0.347554
9	26.30	0.35	23.23	0.338460
10	26.70	0.40	20.35	0.333479
11	28.00	0.25	35.71	0.318284
12	34.00	0.40	20.71	0.263363

Application of 2,6-dimethylpyridinium trinitromethanide {[2,6-DMPyH]C$(NO_2)_3$} as a nanostructured molten salt catalyst

After the synthesis of 2,6-dimethylpyridinium trinitromethanide {[2,6-DMPyH]C$(NO_2)_3$} as a novel nanostructured molten salt catalyst, to optimize the reaction conditions, we confirmed the efficacy of the catalyst in the synthesis of 1,2,4,5-tetrasubstituted imidazole derivatives (Scheme 2). For this purpose, as a model, the condensation reaction of benzil/benzoin, 4-biphenylcarbaldehyde, 4-bromoaniline and ammonium acetate was considered using different amounts of the catalyst in a temperature range of 25–100 °C under solvent-free conditions (Table 2). As Table 2 shows, the best results were achieved when the reaction was attained in the presence of 0.5 mol% of nanostructured molten salt catalyst at room temperature (Table 2, entry 3). In the absence of the catalyst, a low yield of the product was obtained after 1 h (Table 2, entries 1 and 2). Increasing the reaction temperature and catalyst loading did not improve the rate of the reaction (Table 2, entries 4–11).

Table 2 Effect of the amount of the catalyst and temperature on the condensation of benzil/benzoin, 4-biphenylcarbaldehyde, 4-bromoaniline and ammonium acetate under solvent-free conditions[a]

Entry	Catalyst loading (mol%)	Reaction temperature (°C)	Reaction time (min)		Yield[b] (%)	
			Method A	Method B	Method A	Method B
1	—	r.t.	60	60	12	10
2	—	100	60	60	15	12
3	0.5	r.t.	6	8	96	95
4	0.5	50	6	8	96	95
5	0.5	75	6	8	96	95
6	0.5	100	6	8	96	95
7	1	r.t.	6	8	96	95
8	1	100	6	8	96	95
9	2	r.t.	6	8	96	95
10	2	100	6	8	96	95
11	5	r.t.	7	10	95	93
12	5	100	7	10	95	93

[a] Reaction conditions. Method A: benzil (1 mmol), aldehydes (1 mmol), amine derivatives (1 mmol), ammonium acetate (1 mmol); method B: benzoin (1 mmol), aldehydes (1 mmol), amine derivatives (1 mmol), ammonium acetate (1 mmol). [b] Isolated yield.

To compare the competence of the solution *versus* solvent-free conditions, a mixture of benzil/benzoin, 4-biphenylcarbaldehyde, 4-bromoaniline and ammonium acetate, as the model reaction, in the presence of 0.5 mol% of [2,6-DMPyH]-$C(NO_2)_3$ as a novel nanostructured molten salt in various solvents, such as H_2O, C_2H_5OH, CH_3CN, CH_3CO_2Et, CH_2Cl_2, toluene and benzene, was considered at room temperature. The results are summarized in Table 3. As can be seen in Table 3, solvent-free was the best condition in this reaction.

Stimulated by the good results and to confirm the scope of this procedure, various 1,2,4,5-tetrasubstituted imidazole derivatives were synthesized from the four-component condensation reaction of benzil/benzoin, aromatic aldehydes, amine derivatives and ammonium acetate under solvent-free conditions at room temperature in the presence of a catalytic amount of 2,6-dimethylpyridinium trinitromethanide {[2,6-DMPyH]$C(NO_2)_3$}, as a novel nanostructured molten salt catalyst. The results are presented in Table 4. The substituents on the aromatic ring have strong effects on the yields under these reaction conditions. All the aromatic aldehydes and amines containing electron-releasing substituents and electron-withdrawing substituents on their aromatic ring afforded the related products in high to excellent yields and in short reaction times. The reaction times of aromatic aldehydes with electron withdrawing groups were rather faster than those with the electron donating groups, but the reaction times of the aromatic amines with electron releasing groups were faster than those with electron withdrawing groups. Moreover, the reaction in the presence of benzil is faster than that in the presence of benzoin.

Table 3 The effect of different solvents on the reaction of benzil/benzoin, 4-biphenylcarbaldehyde, 4-bromoaniline and ammonium acetate catalyzed by {[2,6-DMPyH]$C(NO_2)_3$} as a novel nanostructured molten salt (0.5 mol%) at room temperature[a]

Entry	Solvent	Reaction time (min)		Yield[b] (%)	
		Method A	Method B	Method A	Method B
1	Solvent-free	6	8	96	95
2	H_2O	10	15	95	93
3	C_2H_5OH	10	15	95	93
4	CH_3CN	15	20	93	90
5	CH_3CO_2Et	25	30	93	90
6	CH_2Cl_2	45	45	25	20
7	Toluene	60	60	20	15
8	Benzene	120	120	20	15

[a] Reaction conditions. Method A: benzil (1 mmol), aldehydes (1 mmol), amine derivatives (1 mmol), ammonium acetate (1 mmol); method B: benzoin (1 mmol), aldehydes (1 mmol), amine derivatives (1 mmol), ammonium acetate (1 mmol). [b] Isolated yield.

The suggested catalytic methods are shown in Fig. S5,† which are in accordance with the literature reports.[25–29] The nanostructured {[2,6-DMPyH]$C(NO_2)_3$} has one acidic hydrogen that can participate in hydrogen bonding. Subsequently, both benzil/benzoin and aromatic aldehydes were activated by {[2,6-DMPyH]$C(NO_2)_3$} to react with nucleophiles. As can be realized in Scheme 3, the nucleophilic attack of amine (2) on the activated carbonyl of aldehydes (7) results in the formation of imine (10), which can be monitored by the nucleophilic attack of the *in situ*-produced ammonia from ammonium acetate to the imine (10), giving the intermediate (11). From the condensation of the intermediate (11) with the activated carbonyl of benzil/benzoin (12) and its dehydration, analogous 1,2,4,5-tetrasubstituted imidazole derivatives (6) are produced. Moreover, the formation of various hydrogen bonds between the substrates and catalyst could simplify a more efficient catalysis in the reaction. High reaction rates could similarly be influenced by the nanostructured catalyst, as discussed in this study.

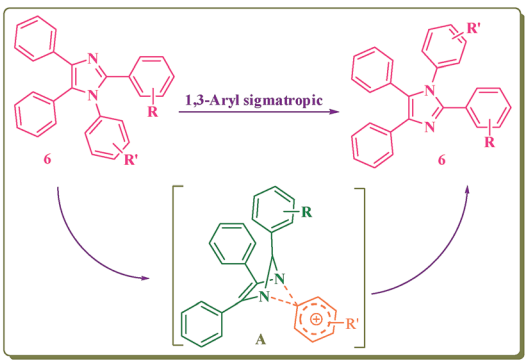
Because of the appropriate symmetry of these compounds *via* 1,3-aryl sigmatropic symmetry,[30,31] almost half of the signals were observed in ^{1}H NMR and ^{13}C NMR spectra (Scheme 3).

Furthermore, the reusability of the nanostructured molten salt catalyst was confirmed upon the condensation of benzil/

Table 4 Synthesis of 1,2,4,5-tetrasubstituted imidazole derivatives in the presence of 0.5 mol% {[2,6-DMPyH]C$(NO_2)_3$} as a nanostructured molten salt catalyst[a]

			Method A		Method B		
Entry	Aldehyde	R′	Time (min)	Yield[b] (%)	Time (min)	Yield[b] (%)	M.p (°C) [Ref.]
1	4-Nitrobenzaldehyde	4-CH_3	1	98	5	96	218–220 [25]
2	4-Nitrobenzaldehyde	4-Cl	3	97	10	95	235–237
3	4-Nitrobenzaldehyde	4-Br	2	98	8	96	262–264
4	4-Chlorobenzaldehyde	4-CH_3	5	96	7	95	224–226 [26]
5	4-Chlorobenzaldehyde	4-Cl	8	95	12	93	209–211 [25]
6	4-Chlorobenzaldehyde	4-Br	7	95	10	94	217–219
7	2,4-Dichlorobenzaldehyde	4-Cl	10	92	15	91	246–248
8	2,4-Dichlorobenzaldehyde	4-Br	8	93	12	92	251–253
9	4-Methylbenzaldehyde	4-Cl	12	92	18	91	221–223 [26]
10	4-Methylbenzaldehyde	4-Br	10	93	15	92	228–230
11	4-Methoxybenzaldehyde	4-Br	10	93	15	92	220–222
12	4-Chloro-3-nitrobenzaldehyde	4-Br	6	94	10	93	223–225
13	4-Biphenylcarbaldehyde	4-Br	6	96	8	95	281–283
14	Naphthalene-2-carbaldehyde	4-Br	7	95	10	94	253–255

[a] Reaction conditions. Method A: benzil (1 mmol), aldehydes (1 mmol), amine derivatives (1 mmol), ammonium acetate (1 mmol); method B: benzoin (1 mmol), aldehydes (1 mmol), amine derivatives (1 mmol), ammonium acetate (1 mmol). [b] Isolated yield.



Scheme 3 The 1,3-aryl sigmatropic symmetry of 1,2,4,5-tetrasubstituted imidazole derivatives.

benzoin, 4-biphenylcarbaldehyde, 4-bromoaniline and ammonium acetate. At the end of the reaction, ethyl acetate was added to the reaction mixture and heated to extract the product and the remaining starting materials. This solution was then washed with water to separate the catalyst from other materials (the product is soluble in hot ethyl acetate, while the nanostructured molten salt catalyst is soluble in water). The aqueous layer was decanted, separated and used for alternative reactions after removing the water. It was found that the catalytic activity of the catalyst was restored within the limits of the experimental errors for five continuous runs (Fig. S6†). The recycled catalyst was also characterized by FTIR, ^{1}H NMR and ^{13}C NMR spectra after its application in the reaction. These spectra were identical to those of the fresh catalyst (Fig. S7–S9†). Moreover, the size of the catalyst was assessed after the recovery procedure by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) analyses. This study showed that the catalyst was recovered in a nano-size. The related images are shown in Fig. S10.†

Conclusions

In summary, a novel, green and eco-friendly nanostructured molten salt catalyst, namely, 2,6-dimethylpyridinium trinitromethanide {[2,6-DMPyH]C$(NO_2)_3$}, was designed, assessed and completely characterized by IR, ^{1}H NMR, ^{13}C NMR, mass spectroscopy, thermal gravimetric analysis (TGA), differential thermal gravimetric (DTG), X-ray diffraction patterns (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) analyses. The catalytic application of [2,6-DMPyH]C$(NO_2)_3$ was considered in the synthesis of 1,2,4,5-tetrasubstituted imidazole derivatives by a four-component condensation reaction of benzil/benzoin, aldehydes, amine derivatives and ammonium acetate under solvent-free conditions at room temperature. Additional studies showed that the nanostructured molten salt acidity plays a key role in the catalyzed reactions. Some different significant advantages of this work are its reasonably cleaner reaction profile, low cost, high yield, short reaction time, reusability of the nanostructured catalyst, simplicity of product isolation and agreement with the green chemistry processes.

Experimental

General procedure for the preparation of the nanostructured molten salt catalyst 2,6-dimethylpyridinium trinitromethanide {[2,6-DMPyH]C$(NO_2)_3$}

To a round-bottomed flask (50 mL) containing 2,6-dimethylpyridine (3 mmol; 0.321 g) in CH_3CN (5 mL), trinitromethane (3.1 mmol; 0.468 g) was added dropwise and heated over a period of 60 min at room temperature. Subsequently, the solvent was removed by distillation under reduced pressure, and the product was dried under vacuum at 80 °C for 120 min. A red solid was prepared (Scheme 1) quantitatively.

2,6-Dimethylpyridinium trinitromethanide {[2,6-DMPyH]-$C(NO_2)_3$}. M.p: 137–139 °C; yield: 98% (0.759 g); spectral data: IR (KBr): ν 3437, 3054, 1634, 1384, cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 2.69 (s, 6H, $-CH_3$), 7.74 (d, 2H, $J = 8.0$ Hz, –CH); 8.37 (t, 1H, $J = 7.8$ Hz, –CH), 9.55 (brs, 1H, –NH); ^{13}C NMR (100 MHz, DMSO-d_6): δ 19.7, 70.2, 125.0, 146.0, 153.5; MS: $m/z = 258$ $[M]^+$, 259 $[M + H]^+$.

General procedure for the synthesis of 1,2,4,5-tetrasubstituted imidazole derivatives

To a mixture of benzil/benzoin (1 mmol), aromatic aldehydes (1 mmol), amine derivatives (1 mmol) and ammonium acetate (1 mmol) in a test tube, 2,6-dimethylpyridinium trinitromethanide was added as a novel nanostructured molten salt catalyst (0.5 mol%), and the subsequent mixture was stirred magnetically under solvent-free conditions at room temperature. After the completion of the reaction, as monitored by TLC with *n*-hexane–ethyl acetate (5 : 2), ethyl acetate (10 mL) was added to the reaction mixture, stirred and refluxed for 3 min, washed with water (10 mL) and decanted to separate the catalyst from the other materials (the reaction mixture was soluble in hot ethyl acetate, while the nanostructured molten salt catalyst was soluble in water). The aqueous layer was decanted and the catalyst was separated after removing the water. The remaining catalyst was used for alternative reactions. The organic layer was evaporated and the crude product was purified by recrystallization from ethanol–water (10 : 1). In this study, the nanostructured molten salt catalyst was recycled and reused five times without significant loss of its catalytic activity.

Spectral data analysis for compounds

2-(4-Nitrophenyl)-4,5-diphenyl-1-*p*-tolyl-1*H*-imidazole (Table 4, entry 1). Yellow solid; M.p: 218–220 °C; yield: (method A: 98%, method B: 96%); IR (KBr): ν 1598, 1505, 1338 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 2.42 (s, 3H, $-CH_3$), 7.23 (t, 3H, $J = 8.4$ Hz, ArH), 7.28 (t, 3H, $J = 6.4$ Hz, ArH), 8.10 (d, 6H, $J = 8.8$ Hz, ArH), 8.36 (d, 6H, $J = 8.8$ Hz, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.1, 112.1, 112.7, 112.8, 112.9, 113.4, 128.2, 128.4, 136.3, 136.5, 145.0, 149.1, 149.2, 151.2, 151.3.

1-(4-Chlorophenyl)-2-(4-nitrophenyl)-4,5-diphenyl-1*H*-imidazole (Table 4, entry 2). Yellow solid; M.p: 218–220 °C; yield: (method A: 97%, method B: 95%); IR (KBr): ν 1624, 1597, 1515, 1343 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.25 (t, 3H, $J = 7.2$ Hz, ArH), 7.43 (t, 3H, $J = 8.8$ Hz, ArH), 8.10 (d, 6H, $J = 8.8$ Hz, ArH), 8.36 (d, 6H, $J = 8.8$ Hz, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 112.0, 112.6, 112.7, 112.9, 113.4, 128.3, 128.4, 136.3, 136.7, 144.6, 149.0, 149.2, 151.2, 151.3; MS: $m/z = 451$ $[M]^+$.

1-(4-Bromophenyl)-2-(4-nitrophenyl)-4,5-diphenyl-1*H*-imidazole (Table 4, entry 3). Yellow solid; M.p: 262–264 °C; yield: (method A: 98%, method B: 96%); IR (KBr): ν 1624, 1596, 1513, 1340 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.18 (t, 3H, $J = 5.8$ Hz, ArH), 7.58 (t, 3H, $J = 5.6$ Hz, ArH), 8.11 (d, 6H, $J = 8.8$ Hz, ArH), 8.36 (d, 6H, $J = 8.8$ Hz, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 124.8, 124.9, 126.3, 128.1, 128.2, 128.5, 128.6, 129.1, 138.5, 142.2, 145.6, 152.1, 152.6, 167.6; MS: $m/z = 495$ $[M]^+$.

2-(4-Chlorophenyl)-4,5-diphenyl-1-*p*-tolyl-1*H*-imidazole (Table 4, entry 4). White solid; M.p: 224–226 °C; yield: (method A: 96%, method B: 95%); IR (KBr): ν 1624, 1580, 1565, 1504 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 2.40 (s, 3H, $-CH_3$), 7.17 (t, 3H, $J = 8.4$ Hz, ArH), 7.24 (t, 3H, $J = 8.0$ Hz, ArH), 7.48 (d, 6H, $J = 8.8$ Hz, ArH), 7.87 (d, 6H, $J = 8.4$ Hz, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.0, 119.7, 123.3, 125.5, 125.9, 126.3, 127.7, 128.1, 128.6, 128.9, 129.5, 138.5, 142.5, 144.9, 149.9.

1,2-Bis(4-chlorophenyl)-4,5-diphenyl-1*H*-imidazole (Table 4, entry 5). Yellow solid; M.p: 209–211 °C; yield: (method A: 95%, method B: 93%); IR (KBr): ν 1625, 1565, 1489, 1084 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.18 (d, 6H, $J = 8.8$ Hz, ArH), 7.39 (t, 3H, $J = 8.8$ Hz, ArH), 7.49 (t, 3H, $J = 8.4$ Hz, ArH), 7.87 (d, 6H, $J = 8.4$ Hz, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 111.5, 124.7, 124.8, 126.2, 126.3, 128.5, 128.6, 129.1, 129.2, 138.4, 138.5, 142.3, 142.7, 145.8.

1-(4-Bromophenyl)-2-(4-chlorophenyl)-4,5-diphenyl-1*H*-imidazole (Table 4, entry 6). White solid; M.p: 217–219 °C; yield: (method A: 95%, method B: 94%); IR (KBr): ν 1622, 1567, 1488, 1089 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.12 (d, 6H, $J = 5.8$ Hz, ArH), 7.49 (t, 3H, $J = 5.4$ Hz, ArH), 7.54 (t, 3H, $J = 5.8$ Hz, ArH), 7.86 (d, 6H, $J = 5.4$ Hz, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 104.0, 111.7, 112.2, 115.5, 119.6, 122.6, 129.2, 130.0, 132.3, 134.4, 137.7, 150.6, 159.2, 177.2; MS: $m/z = 484$ $[M]^+$.

1-(4-Chlorophenyl)-2-(2,4-dichlorophenyl)-4,5-diphenyl-1*H*-imidazole (Table 4, entry 7). White solid; M.p: 246–248 °C; yield: (method A: 92%, method B: 91%); IR (KBr): ν 1614, 1576, 1486, 1384, 1091 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.37 (t, 3H, $J = 5.8$ Hz, ArH), 7.50 (t, 3H, $J = 5.8$ Hz, ArH), 7.59 (d, 6H, $J = 5.6$ Hz, ArH), 7.80 (s, 1H, ArH), 8.16 (d, 4H, $J = 8.4$ Hz, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 110.0, 112.9, 117.1, 117.4, 122.5, 123.1, 124.6, 125.5, 129.4, 133.5, 134.1, 142.7, 152.5, 155.5, 158.7, 158.9; MS: $m/z = 474$ $[M]^+$.

1-(4-Bromophenyl)-2-(2,4-dichlorophenyl)-4,5-diphenyl-1*H*-imidazole (Table 4, entry 8). White solid; M.p: 251–253 °C; yield: (method A: 93%, method B: 92%); IR (KBr): ν 1612, 1585, 1482, 1365, 1096 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.30 (t, 3H, $J = 5.8$ Hz, ArH), 7.60 (d, 6H, $J = 5.4$ Hz, ArH), 7.64 (t, 3H, $J = 5.8$ Hz, ArH), 7.80 (s, 1H, ArH), 8.16 (d, 4H, $J = 8.4$ Hz, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 123.2, 123.4, 123.7, 124.4, 124.6, 125.5, 127.6, 127.7, 128.9, 129.5, 132.7, 133.2, 134.3, 136.4, 143.2, 152.6; MS: $m/z = 518$ $[M]^+$.

1-(4-Chlorophenyl)-4,5-diphenyl-2-*p*-tolyl-1*H*-imidazole (Table 4, entry 9). Yellow solid; M.p: 221–223 °C; yield: (method A: 92%, method B: 91%); IR (KBr): ν 1623, 1598, 1516, 1338, 1106 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 2.42 (s, 3H, $-CH_3$), 7.23 (t, 3H, $J = 8.4$ Hz, ArH), 7.27 (t, 3H, $J = 8.4$ Hz, ArH), 8.11 (d, 6H, $J = 8.8$ Hz, ArH), 8.36 (d, 6H, $J = 8.8$ Hz, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.1, 113.4, 114.0, 115.0, 118.0, 118.1, 134.7, 137.0, 151.8, 152.6, 152.8, 152.9, 153.1, 160.1, 164.6.

1-(4-Bromophenyl)-4,5-diphenyl-2-*p*-tolyl-1*H*-imidazole (Table 4, entry 10). White solid; M.p: 228–230 °C; yield: (method A: 93%, method B: 92%); IR (KBr): ν 1622, 1605, 1474, 1165 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 2.45 (s, 3H, $-CH_3$), 7.11 (t, 3H, $J = 8.8$ Hz, ArH), 7.32 (d, 6H, $J = 8.0$ Hz, ArH), 7.53 (t, 3H, $J = 8.4$ Hz, ArH), 7.81 (d, 6H, $J = 8.0$ Hz, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.7, 127.5,

127.6, 128.3, 128.8, 129.3, 129.5, 137.6, 138.2, 140.7, 140.8, 145.0, 145.9, 147.3, 152.0; MS: $m/z = 464$ $[M]^+$.

1-(4-Bromophenyl)-2-(4-methoxyphenyl)-4,5-diphenyl-1*H*-imidazole (Table 4, entry 11). White solid; M.p: 220–222 °C; yield: (method A: 93%, method B: 92%); IR (KBr): ν 1620, 1605, 1572, 1508, 1254, 1167 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 3.90 (s, 3H, $-OCH_3$), 7.02 (d, 6H, $J = 8.8$ Hz, ArH), 7.10 (t, 3H, $J = 8.8$ Hz, ArH), 7.52 (t, 3H, $J = 8.8$ Hz, ArH), 7.87 (d, 6H, $J = 8.8$ Hz, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.5, 110.0, 115.3, 115.4, 115.5, 123.3, 126.2, 126.3, 126.4, 128.1, 129.3, 133.8, 141.3, 144.4, 144.8; MS: $m/z = 480$ $[M]^+$.

1-(4-Bromophenyl)-2-(4-chloro-3-nitrophenyl)-4,5-diphenyl-1*H*-imidazole (Table 4, entry 12). Yellow solid; M.p: 223–225 °C; yield: (method A: 94%, method B: 93%); IR (KBr): ν 1622, 1599, 1557, 1528, 1353 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.16 (t, 3H, $J = 7.2$ Hz, ArH), 7.57 (t, 3H, $J = 5.6$ Hz, ArH), 7.70 (d, 6H, $J = 8.4$ Hz, ArH), 8.08 (d, 4H, $J = 5.2$ Hz, ArH), 8.43 (s, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 104.6, 112.7, 112.9, 113.5, 120.7, 122.6, 125.3, 129.6, 132.4, 132.5, 132.6, 135.9, 149.5, 156.2, 167.6, 174.8; MS: $m/z = 529$ $[M]^+$.

2-(Biphenyl-4-yl)-1-(4-bromophenyl)-4,5-diphenyl-1*H*-imidazole (Table 4, entry 13). Yellow solid; M.p: 281–283 °C; yield: (method A: 96%, method B: 95%); IR (KBr): ν 1620, 1604, 1485, 1166 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.16 (t, 3H, $J = 7.2$ Hz, ArH), 7.44 (t, 3H, $J = 7.8$ Hz, ArH), 7.50 (d, 2H, $J = 8.0$ Hz, ArH), 7.56 (t, 3H, $J = 8.4$ Hz, ArH), 7.69 (d, 4H, $J = 8.4$ Hz, ArH), 7.75 (d, 4H, $J = 8.4$ Hz, ArH), 8.00 (d, 4H, $J = 8.4$ Hz, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 116.1, 116.2, 116.3, 116.4, 117.2, 117.4, 123.2, 124.6, 125.5, 129.6, 132.8, 134.2, 143.3, 152.5, 155.2, 155.7, 155.8, 176.1; MS: $m/z = 526$ $[M]^+$.

1-(4-Bromophenyl)-2-(naphthalen-2-yl)-4,5-diphenyl-1*H*-imidazole (Table 4, entry 14). Yellow solid; M.p: 253–255 °C; yield: (method A: 95%, method B: 94%); IR (KBr): ν 1617, 1574, 1484, 1331, 1068 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.19 (d, 4H, $J = 7.2$ Hz, ArH), 7.57 (d, 4H, $J = 7.0$ Hz, ArH), 7.59 (t, 2H, $J = 4.0$ Hz, ArH), 7.62 (d, 2H, $J = 8.4$ Hz, ArH), 7.94 (t, 2H, $J = 7.2$ Hz, ArH), 7.97 (t, 4H, $J = 8.8$ Hz, ArH), 8.18 (d, 2H, $J = 5.0$ Hz, ArH), 8.23 (s, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 123.1, 123.2, 123.8, 123.9, 124.0, 126.1, 126.8, 126.9, 127.1, 127.9, 128.9, 129.6, 129.7, 129.8, 132.9, 134.2, 134.7, 134.8, 138.1, 143.5; MS: $m/z = 500$ $[M]^+$.

Acknowledgements

The authors gratefully acknowledge the Bu-Ali Sina University Research Council and Center of Excellence in Development of Environmentally Friendly Methods for Chemical Synthesis (CEDEFMCS) for providing support to this work.

Notes and references

1 (*a*) H. Debus, *Liebigs Ann. Chem.*, 1858, **107**, 199; (*b*) A. Khazaei, M. A. Zolfigol, A. R. Moosavi-Zare, A. Zare, A. Parhami and A. Khalafi-Nezhad, *Appl. Catal., A*, 2010, **386**, 179; (*c*) M. A. Zolfigol, A. Khazaei, A. R. Moosavi-Zare, A. Zare and V. Khakyzadeh, *Appl. Catal., A*, 2011, **400**, 70; (*d*) A. Khazaei, M. A. Zolfigol, A. R. Moosavi-Zare, F. Abi, A. Zare, H. Kaveh, V. Khakyzadeh, M. Kazem-Rostami, A. Parhami and H. Torabi-Monfared, *Tetrahedron*, 2013, **69**, 212; (*e*) A. Khazaei, F. Gholami, V. Khakyzadeh, A. R. Moosavi-Zare and J. Afsar, *RSC Adv.*, 2015, **5**, 14305.

2 J. G. Lambardino and E. H. Wiesman, *J. Med. Chem.*, 1974, **17**, 1182.

3 I. Lantos, W. Y. Zhang, X. Shui and D. S. Eggleston, *J. Org. Chem.*, 1993, **58**, 7092.

4 R. Conssoni, P. D. Croce, R. Ferraccioli and L. Rosa, *J. Chem. Res.*, 1991, 188.

5 C. Zhang, E. J. Moran, T. F. Woiwode, K. M. Short and A. M. M. Mjalli, *Tetrahedron Lett.*, 1996, **37**, 751.

6 V. Stocek and W. Schunack, *Arch. Pharm.*, 1974, **307**, 922.

7 C. F. Claiborne, N. J. Liverton and K. T. Nguyen, *Tetrahedron Lett.*, 1998, **39**, 8939.

8 A. F. Pozherskii, A. T. Soldalenkov and A. R. Katritzky, *Heterocycles in Life, Society*, Wiley, New York, 1997, p. 179.

9 S. E. Wolkenberg, D. D. Wisnosk, W. B. Liester, Y. Wang, Z. Zhao and C. W. Lindsley, *Org. Lett.*, 2004, **6**, 1453.

10 R. Liebi, R. Randte, H. Mildenberger, K. Bauer and H. Bieringer, *Chem. Abstr.*, 1987, **108**, 6018g.

11 A. P. Philips, H. L. White and S. Rosen, *Eur. Pat. Appl.*, 1983, **58**, 890.

12 T. Welton, *Chem. Rev.*, 1999, **99**, 2071.

13 K. R. Seddon, A. Stark and M. J. Torres, *Pure Appl. Chem.*, 2000, **72**, 2275.

14 J. Dupont, R. F. de Souza and P. A. Z. Suarez, *Chem. Rev.*, 2002, **102**, 3667.

15 J. G. Huddleston, H. D. Willauer, R. P. Swatloski, A. E. Visser and R. D. Rogers, *Chem. Commun.*, 1998, 1765.

16 A. E. Visser, R. P. Swatloski and R. D. Rogers, *Green Chem.*, 2000, **2**, 1.

17 M. L. Dietz and J. A. Dzielawa, *Chem. Commun.*, 2001, 2124.

18 A. E. Visser, J. D. Holbrey and R. D. Rogers, *Chem. Commun.*, 2001, 2484.

19 *Polymer Electrolytes Reviews*, ed. J. R. MacCallum and C. A. Vincent, Elsevier, London, 1987, vol. 1.

20 *Polymer Electrolytes Reviews*, ed. J. R. MacCallum and C. A. Vincent, Elsevier, London, 1989, vol. 2.

21 N. Gokon, Y. Oku, H. Kaneko and Y. Tamaura, *Sol. Energy*, 2002, **72**, 243.

22 M. Kusche, F. Agel, N. N. Bhriain, A. Kaftan, M. Laurin, J. Libuda and P. Wasserscheid, *ChemSusChem*, 2014, **7**, 2516.

23 (*a*) M. B. Gawande and P. S. Branco, *Green Chem.*, 2011, **13**, 3355; (*b*) A. Khazaei, A. R. Moosavi-Zare, Z. Mohammadi, A. Zare, V. Khakyzadeh and G. Darvishi, *RSC Adv.*, 2013, **3**, 1323; (*c*) A. R. Moosavi-Zare, Z. Asgari, A. Zare, M. A. Zolfigol and M. Shekouhy, *RSC Adv.*, 2014, **4**, 60636.

24 C. J. Li and L. Chen, *Chem. Soc. Rev.*, 2006, **35**, 68.

25 A. Karimi, R. Alimohammadi, Z. Azizian, J. Mohammadi and A. A. Mohammadizadeh, *Catal. Commun.*, 2006, **7**, 728.

26 K. Sivakumar, A. Kathirvel and A. Lalitha, *Tetrahedron Lett.*, 2010, **51**, 3018.

27 A. Zare, F. Abi, A. R. Moosavi-Zare, M. H. Beyzavi and M. A. Zolfigol, *J. Mol. Liq.*, 2013, **178**, 113.

28 A. R. Moosavi-Zare, M. A. Zolfigol, V. Khakyzadeh, C. Böttcher, M. H. Beyzavi, A. Zare, A. Hasaninejad and R. Luque, *J. Mater. Chem. A*, 2014, **2**, 770.
29 M. A. Zolfigol, A. Khazaei, A. R. Moosavi-Zare, A. Zare, Z. Asgari, V. Khakyzadeh and A. Hasaninejad, *J. Ind. Eng. Chem.*, 2013, **19**, 721.
30 S. Hou, X. Li and J. Xu, *J. Org. Chem.*, 2012, **77**, 10856.
31 A. Gomez-Zavaglia, A. Kaczor, R. Almeida, M. L. S. Cristiano, M. E. S. Eusebio, T. M. R. Maria, P. Mobili and R. Fausto, *J. Phys. Chem. A*, 2009, **113**, 3517.