Functionalized 1,5,7-triazabicyclo [4.4.0] dec-5-ene (TBD) as Novel Organocatalyst for Efficient Depolymerization of Polyethylene Terephthalate (PET) Wastes

SIMONA NICA[1], MONICA DULDNER[2], ANAMARIA HANGANU[1,3], STELA IANCU[2], BOGDAN CURSARU[2], ANDREI SARBU[2], PETRU FILIP[1], EMERIC BARTHA[1]*

[1]Institute of Organic Chemistry C.D. Nenitzescu of the Romanian Academy, 202B Splaiul Independentei, 060023, Bucharest, Romania

[2]National Institute of Research and Development for Chemistry and Petrochemistry-ICECHIM, 202 Splaiul Independentei, 060041, Bucharest, Romania

[3]University of Bucharest, Faculty of Chemistry, Department of Organic Chemistry, Biochemistry and Catalysis, 90-92 Sos. Panduri, 050657, Bucharest, Romania

Poly(ethyleneterephthalate) waste was efficiently depolymerized through glycolysis and aminolysis reactions in the presence of functionalized 1,5,7-triazabicyclo [4.4.0] dec-5-ene (TBD) catalyst. The new catalyst of monoamide-ester type, was synthesized through reaction of dimethylterephthalate (DMT) with TBD in refluxing benzene. It was developed as a consequence of the mechanistic investigations of the transesterification reaction of isosorbide with DMT. To test the stability of functionalized TBD compound towards possible amide bond breakage, reactions with primary and secondary glycols as well as primary amines were performed when only the carboxymethyl group reacted. Moreover, it was found that the depolymerization of poly(ethyleneterephthalate) wastes proceeds faster in the presence of this novel organocatalyst by comparison with the hygroscopic TBD precursor.

Keywords: organocatalysis; glycolysis; aminolysis; PET recycling

Chemical recycling of PET is of increased interest in the scientific comunity since it reduces the amount of waste sent to landfill as well as the use of polymers obtained from petrol based feedstock. In addition, a full recovery of the monomers which can be used for the preparation of new polymeric materials or as intermediates for other industrial applications is possible [1]. Depending on the depolymerizing agent, the chemical recycling of PET waste can be carried out for obtaining monomers such as terephthalic acid (TPA), ethylene glycol (EG), bis(2-hydroxyethyl)terephthalate (BHET) and dimethyl terephthalate (DMT) [2-4]. These products can be obtained through hydrolysis, glycolysis and methanolysis of PET wastes. In addition, aminolysis or ammonolysis of the polymer affords valuable monomers which are relevant for production of polyurethane [5,6]. However, the feasibility of the chemolytic depolymerization of PET waste is quite low at the moment due to the harsh reaction conditions required for the polymer scission as well as due the contamination of the products with metal salts from the used catalysts [7-9]. Organic catalysts were reported as attractive alternatives to traditional organometallic salts due to low working temperature and selective polymerization/depolymerization reactions [10-16]. The feasibility of the chemolytic depolymerization of PET waste can be further improved using biomass derived diols as depolymerizing reagent. A nice example is the isosorbide, a diol with rigid structure that offers various applications of the resulting materials [17]. However, a major drawback that limits its use as depolymerizing agent is related to the low reactivity of the secondary alcohol [18]. The isosorbide-mediated glycolysis of PET waste is generally conducted at 250 °C using $Ti(OBu)_4$ as catalyst, temperature at which the diol is colouring when exposed for long time [19]. Therefore, the development of effective catalytic systems for improving the existent harsh reaction conditions is highly desirable. We have previously reported on the use of isosorbide as glycolysis reagent of PET waste using organic catalysis [20,21]. Mechanistic investigations of the transesterification reaction of isosorbide with dimethyl terephthalate, monomer formed by methanolysis of PET polymer revealed the formation of a covalently bonded adduct when TBD is used as catalyst [21]. This new compound is represented by methyl 4-(2,3,4,6,7,8-hexahydro-1H-pyrimido[1,2-a]pyrimidine-1-carbonyl), **1**, which is formed at low temperature. Herein, we will present the results of the investigations regarding the reactivity of this novel compound with various diols and primary amines as well as its performances as catalyst for both glycolysis and aminolysis of PET wastes.

Experimental part

Materials and instruments

The catlytic reactions were carried out under inert atmosphere. PET waste was obtained from post-consumer bottles, cut into small flakes and cleaned thoroughly by washing with water containing detergent and then with distilled water. The cleaned PET waste flakes were dried at 80°C for several hours prior to use. 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), ethylene glycol (EG; anhydrous, 99.8%), propylene glycole, ethanol amine, ethylendiamine and the involved solvents were purchased from Sigma-Aldrich and used as received. All Nuclear Magnetic Resonance (^1H and ^{13}C NMR) measurements were recorded on Bruker 300 and 500 MHz spectrometers, at room temperature in deuterated solvents: benzene-d6 (C_6D_6), chloroform-d ($CDCl_3$), CD_3COOD and deuterated dimethylsulfoxide (DMSO-d_6). Melting points were

* email: bimre@ccocdn.ro, Phone: + 4021316 79 00

determined with Koehler Automatic Melting Point Range Apparatus (K90190).

Reactions of methyl 4-(2,3,4,6,7,8-hexahydro-1H-pyrimido [1,2-a]pyrimidine-1-carbonyl) benzoate, 1 *at low temperature* (scheme 1)

Reaction with diols

Compound **1** (30 mg, 0.1 mmol) and two equivalents of either EG, propylene glycol (PG) or isosorbide (IS) were dissolved in benzene (5 mL) and heated under reflux for 4 h. After removal of the solvent, the resulting compound was redissolved in $CDCl_3$ and subjected to ^{1}H-NMR investigations.

Compound **2**, formed by reaction with EG was isolated in pure form after crystallization and trituration with diethyl ether for which 2-hydroxyethyl-4-(2,3,4,6,7,8-hexahydro-1H-pyrimido[1,2a]pyrimidine-1-carbonyl)benzoate chemical structure was assigned. The analysis data are the following: 100 %, m.p. 240°C (descomp.); ^{1}H NMR (300 MHz, $CDCl_3$, δ): 8.02 (d, 2H, J = 8.4 Hz, H^a), 7.97 (d, 2H, J = 8.1 Hz, H^b), 4.37 (m, 2H, CH_2OCO), 3.86 (m, 2H, CH_2OH), 3.62 (s, 1H, OH), 3.28 (t, 4H, J = 5.7 Hz, CH_2^c), 3.18 (t, 4H, J = 6.0 Hz, CH_2^d), 1.91 (m, 4H, CH_2^e).

For PG reagent, the reaction occurs with 60 % conversion of isomers mixture resulting compound **3a** by carbonyl bonding of the primary hydroxyl group and compound **3b** by reaction with secondary hydroxyl group. Compound **3a**: 2-hydroxypropyl 4-(2,3,4,6,7,8-hexahydro-1H-pyrimido[1,2-a]pyrimidine-1-carbonyl)benzoate; ^{1}H-NMR (300 MHz, $CDCl_3$, δ): 7.96-8.06 (m, 4H, Ar-H); 4.13 (m, 1H,CH^aH^bO); 3.72(m, 1H, CH^aH^bO); 3.70 (m, 1H, CHOH); 1.22(CH_3) 3,30 (m, 4H, CH_2^c), 3.20 (m, 4H, CH_2^d), 1.93 (m, 4H, CH_2^e)); ^{13}C-NMR (75 MHz, $CDCl_3$, δ): 173.4 (CO-O), 167.2 (CO-NH), 151.7 (Cq, guanidine), 142.3 (Cq, *ipso*), 131.0 (Cq, *ipso*), 129,13 (C^a), 128.99 (C^b), 70.21 (CH_2O); 65.70 (CHOH); 46.9 (C^c), 37.59 (C^d), 20.9 (C^e), 19.29 (CH_3)) .

Compound **3b**: 1-hydroxypropan-2-yl 4-(2,3,4,6,7,8-hexahydro-1H-pyrimido[1,2-a]pyrimide-1-carbonyl)benzoate, ^{1}H-NMR(300 MHz, $CDCl_3$, δ): 7.96-8.06 (m, 4H, Ar-H); 4,27(m, 1H, CHOAr); 3.55 (m, 1H, CH^aH^b-OH); 3.32 (m, 1H, CH^aH^b-OH); 1.30 (CH_3); 3,30 (m, 4H, CH_2^c), 3.20 (m, 4H, CH_2^d), 1.93 (m, 4H, CH_2^e); 16.20 (CH3) ^{13}C-NMR (75 MHz, $CDCl_3$, δ): 173.4 (CO-O), 167.2 (CO-NH), 151.7 (Cq, guanidine), 142.3 (Cq, *ipso*), 131.0 (Cq, *ipso*), 129,13 (C^a), 128.99 (C^b), 73.03 (CHOAr); 65.23 (CH_2OH); 46.9 (C^c), 37.59 (C^d), 20.9 (C^e), 16.20 (CH_3). The **3a/3b** molar ratio is 2/1, similar to our previous reported results.

Isosorbide reacted much slower with 30 % conversion after four hours resulting in a mixture of terephthalates formed by carbonyl binding at exo hydroxyl group, **4a**, (3R, 3aR, 6S,6aR)-6-hydroxyhexahydrofuro[3,2-b]furan-3-yl-4-(2,3,4,6,7,8-hexahydro-1H-pyrimido[1,2-a] pyrimidi-ne-1-carbonyl)benzoate, ^{1}H-NMR: 5.39 (m, 1H, exo-ester); 4.65 (m, 1H, CH^4-IS) ppm and at endo hydroxyl group, repectively, **4b**, (3S, 3aR, 6R, 6aR)- 6-hydroxy-hexahydrofuro[3,2-b]furan-3-yl-4-(2,3,4,6,7,8-hexahydro-1H-pyrimido[1,2-a]pyrimidine-1-carbonyl)benzoate, ^{1}H-NMR: 5.30 (m, 1H, endo-ester); 4.89 (m, 1H, CH^3-IS) ppm. The *exo*/*endo* ratio is 55/45, similar to one observed for isosorbide mediated glycolysis of PET.

Reaction with amines

Compound **1** (30 mg, 0.1 mmol) and either ethanolamine (EA) (16.3 mg, 0.267 mmol) or ethylene-diamine (EDA) (21.6 mg, 0.205 mmol) were dissolved in benzene (5 mL) and heated under reflux for 4 h. After removal of the solvent, the resulting solid material was redissolved in $CDCl_3$.

Reaction with EA yielded compound **5**, 4-(2,3,4,6,7,8-hexahydro-1H-pyrimido [1,2a]pyrimidine-1-carbonyl)-N-(2-hydroxyethyl) bezamide. ^{1}H-NMR (300 MHz, $CDCl_3$, δ): 8.06 (t, 1H, J = 5.4 Hz, NH), 7.98 (d, 2H, J = 8.1 Hz, H^a), 7.78 (d, 2H, J = 8.1 Hz, H^b), 3.76 (m, 2H, CH_2NH), 3.62 (s, 1H, OH), 3.56 (m, CH_2OH), 3.25 (t, J = 5.7 Hz, CH_2^c), 3.17 (t, J = 5.7 Hz, CH_2^d), 1.90 (m, 4H, CH_2^e) ppm.

From reaction with EDA, compound **6**, N-(2-aminoethyl)-4-(2,3,4,6,7,8-hexahydro-1H-pyrimido[1,2a]pyrimidine-1-carbonyl) benzamide was obtained. ^{1}H-NMR (300 MHz, $CDCl_3$, δ): 8.08 (d, 2H, H^a), 7.79 (m, 2H, H^b), 3.47 (m, 2H, CH_2NH), 3.33 (t, J = 5.7 Hz, CH_2^c), 3.26 (t, J = 6.0 Hz, CH_2^d), 2.90 (m, 2H, CH_2NH_2), 1.98 (m, 4H, CH_2^e).

Catalytic activity of compound 1 at high temperature (scheme 2)

Glycolysis

PET waste (480 mg, 2.5 mmol) was reacted with EG (2.1 mL, 37.5 mmol, 15 eq) in the presence of compound **1** (75 mg, 0.25 mmol) at 190 °C until a clear homogenous solution is formed. The product was analyzed by NMR spectrometry (fig. S14 and S15, Supp. Info). The resulting monomer is *bis*(2-hydroxyetil)terephtalate (BHET): ^{1}H-NMR (500 MHz, DMSO-d_6, δ): 8.11 (s, 4H, H_{arom}), 4.98 (t, 1H, J = 5.4 Hz, OH), 4.48 (s, EG), 4.31 (m, 4H, CH_2-OCO), 3.70 (m, 4H, CH_2-OH). The same protocol was followed for glycolysis of PET waste with isosorbide. The data are listed in table 1.

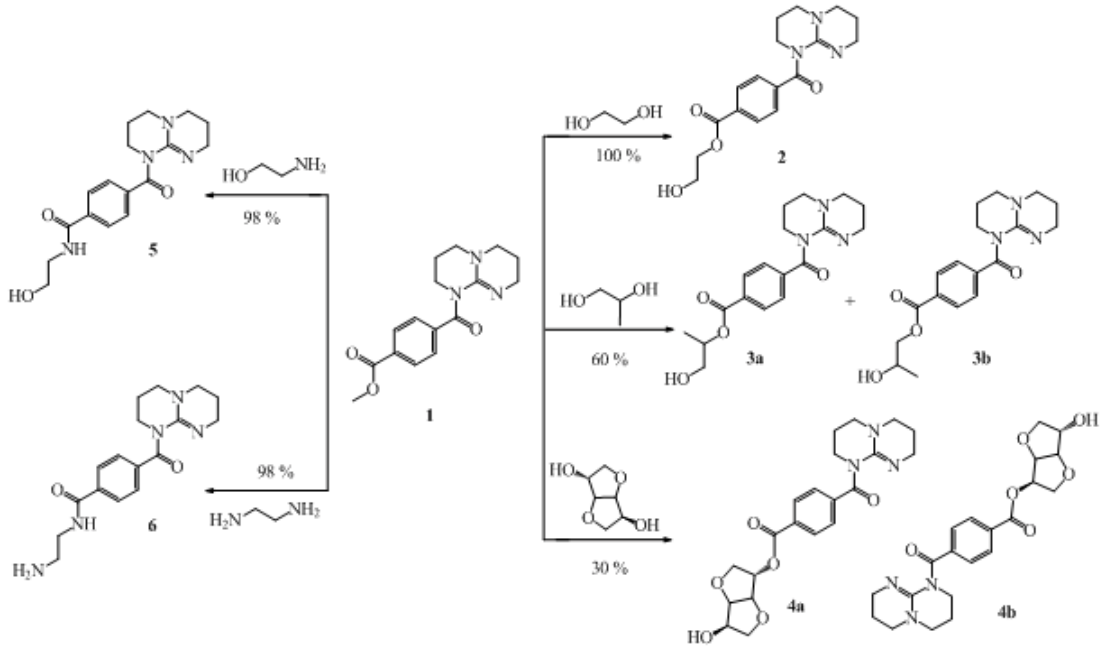
Aminolysis

The procedure was similar with the glycolysis described above using PET waste (480 mg, 2.5 mmol), ethanolamine (1.0 mL, 11.5 mmol) and compound 1 (75 mg, 0.25 mmol) at 190 °C for 2 - 3 min, when a clear solution is observed. A white crystalline solid was formed for which the ^{1}H-NMR spectrum is in accordance with the formation of *bis*(2-hydroxyetil)terephtalamide (BHETA); ^{1}H-NMR: (500 MHz, DMSO-d_6, δ): 8.57 (t, 2H, J = 5.0 Hz, NH), 7.87 (s, 4H, H_{arom}), 4.97 (t, 1H, J = 5.1 Hz, OH), 3.52 (m, 4H, CH_2-NH), 3.37 (m, 4H, CH_2-OH) ppm. ^{13}C-NMR (125 MHz, DMSO-d_6, δ): 166.67 (Cq^{amide}, C=O); 137.07 (Cq^{ipso} C=O); 127.66 (CH^{Ar}); 60.04 (CH_2OH); 42.60 (CH_2NH) ppm.

When ethylenediamine (1.5 g, mmol) was used for depolymerization of PET waste (0.48 g, 2.5 mmol) at 120 °C (the boiling point of EDA), the reaction was complete in 10 min forming *bis*(2-aminoethyl)terephthalamide (BAET); ^{1}H-NMR (300 MHz, CD_3COOD, δ): 7.83 (s, 4H, CH^{Ar}); 3.62(m, 4H, CH_2NH); 3.24(m, 4H, CH_2NH_2); ^{13}C-NMR (75 MHz, CD_3COOD, δ): 170.91 (Cq^{amide}); 138.12 (Cq^{ipso} C=O); 129.58 (CH^{Ar}); 41.76 (CH_2NH); 39.57 (CH_2NH_2) ppm.

Results and disscussions

The reactivity of the covalently bonded TBD adduct was investigated following two reactions type: i) the possible acyl-transfer in the reaction with different diols and/or amine based on the easy formation of amide-ester, **1** (scheme 1) and ii) reactions of DMT with various diols in presence or absence of **1** in the same conditions when a covalently bonded adduct is formed. The used diols were those currently involved in the glycolysis of PET waste containing hydroxyl groups of different reactivity: primary OH in ethylene glycol, primary and secondary in propylene glycol and all secondary in isosorbide. For competitive reaction between amino and hydroxyl groups, ethylenediamine and ethanolamine were also tested. The acyl-transfer reactions were performed in anhydrous benzene, under reflux using 2-3 equivalents of diol or amine for one equivalent of adduct. The reactions run for four hours, the conversion being shown in scheme 5. The crude



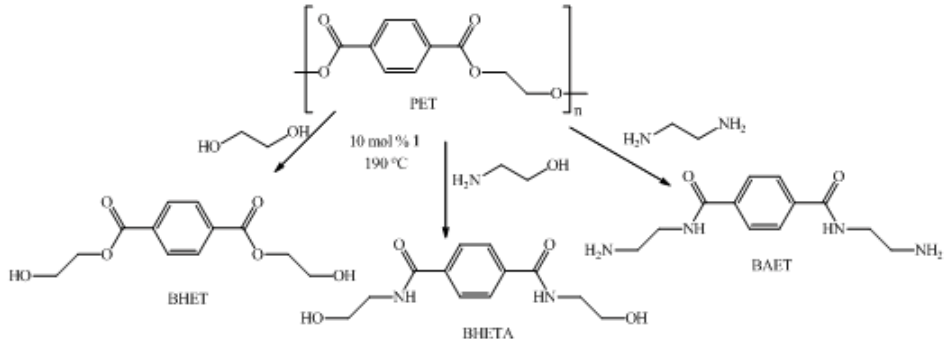
Scheme 1. Reactions of compound 1 with diols and primary amines as possible *acyl intermediate* of the transesterification reaction.

products obtained after benzene removal were analyzed by NMR spectroscopy. In all cases, besides the diol chemical shifts, two new signals corresponding to ethylene protons belonging to the diol/amine reactants were observed. The aromatic protons appear as AB quartet presenting different chemical shifts by comparison with the starting TBD-adduct. Analysis of the integration data revealed without exception that, the glycol/terephthalate/TBD ratio is 1:1:1. The structural assignment was established by comparison with ^{1}H-NMR spectra of products formed by PET glycolysis (BHET and/or other IS-glycolizate). Based on these data we can affirm that instead of the amide breakage, a transesterification reaction involving the carbomethoxy group occurred. Extended reaction time to 24 h does not change the mechanistic results, the only improvement being the increased conversion of the less reactive diols to form the compounds shown in scheme 1. Thus, the reaction of **1** with ethylene glycol led to the formation of 2-hydroxyethyl-4-(2,3,4,6,7,8-hexahydro-1H-pyrimido[1,2a]pyri-midine-1-carbonyl)benzoate, **2**. The structural assignment of **2** is confirmed by the presence of the methylene protons of the ethylene glycol, upfielded for the CH_2-OCO at 4.37 ppm and 3.86 ppm for the CH_2-OH, respectively. The reaction is quantitative within 4 h. Further on, **1** was reacted with propylene glycol which posses two hydroxyl groups of different reactivity. In this case, the reaction also supposes a transesterification of the carboxymethyl group involving both hydroxyl groups of the diol and obtaining compounds **3a** and **3b**, respectively. However, the reaction is slower, the amount of reacted propylene glycol being around 60 %. Although performed in the same conditions as previously described (refluxing benzene), in the case of the less reactive hydroxyl groups, as in isosorbide, the reaction hardly took place. The amount of reacted isosorbide does not exceed 30% and as in the previous cases it supposes only the transesterification of the carboxymethyl group (scheme 1, compound **4**).

In order to see what will happen when competitive amino and hydroxyl groups are present in the same molecule, we have monitored the reaction of the covalently bonded adduct, **1**, with ethanolamine. To our surprise, although no amide breakage in the intermediate **1** occurred, an aminolysis reaction between the carboxymethyl and primary amine took place (compound **5**, scheme 1). This was assigned based on the ^{1}H-NMR spectrum where, the NH proton resonates at 8.06 ppm. Analysis of the chemical shifts belonging to the methylene protons and comparison with their resonances in the starting ethanolamine revealed that the reaction only occurs at the amino group. Similar reactivity was observed when compound **1** was reacted with ethylenediamine forming compound, **6** in quantitative yield. The terephthalate protons resonated as two distinct doublets in accordance with their non-equivalent structure in the resulting compounds, whereas the aliphatic protons and the TBD methylene protons resonated in the expected area.

Catalytic activity of the covalently bonded intermediate at high temperature

On the grounds that the PET waste glycolysis and/or aminolysis occur at high temperature, compound **1** was investigated as possible catalyst of these two reactions at temperature up to 190 °C (scheme 2). In the case of PET waste glycolysis with ethylene glycol, 10 mol % of **1**, catalyzed the depolymerisation of the polymer within 45



Scheme 2. Depolymerization of PET waste with diols and primary amine catalyzed by 10 mol % of compound **1**

Entry	Catalyst	Reactant	Conversion (%)	Reaction time (min)	Product	
					Monomer (%)	Dimer (%)
1[a]	**1**	EG	100.0	45.0	93 (BHET)	7
2[a]	TBD	EG	100.0	120.0	94 (BHET)	6
3[a]	**2**	EG	100.0	65.0	91 (BHET)	9
4[b]	**2**	EG	-	240.0	No reaction	
5[a]	DBU	EG	100.0	90.0	94 (BHET)	6
6[c]	**1**	IS	65.0	240.0	Not determined	
7[c]	TBD	IS	50.0	240.0	Not determined	
8[d]	**1**	EA	100.0	3.0	100 (BHETA)	
9[e]	**1**	EDA	100.0	10.0	100 (BAET)	

[a]PET/EG molar ratio of 1/15. [b]no PET was used. [c]PET/IS molar ratio of 1/2. [d]PET/EA molar ratio of 1/5. [e]PET/EDA molar ratio of 1/15

Table 1
COMPARATIVE CATALYTIC ACTIVITY OF COMPOUND 1 WITH THE PARENT TBD FOR GLYCOLYSIS AND AMINOLYSIS OF PET WASTES

minutes at 190°C. The reaction was monitored visually until no pellet was present. The ^{1}H-NMR analysis shows the formation of BHET as major compound.

For testing the catalytic efficiency of compound **1**, a parallel glycolytic depolymerization reaction using commercially available catalysts such as TBD and DBU, was performed under the same reaction conditions. The TBD catalyzes the glycolysis of PET waste within 120 minutes, whereas with DBU, the depolymerization reaction is complete within 90 min. For a better view of the catalytic reaction, we also tested the intermediate **2** for glycolysis of PET waste. While no reaction occurs between **2** and EG (table 1, entry 3), the PET waste is depolymerized within 65 min with formation of 91 % BHET together with 9 % dimmers (table 1, entry 2). When isosorbide was used for PET glycolysis, compound **1** also performs better than commercially available TBD parent, the conversion being 65 % as compared to 50 % within 240 min.

When the aminolysis reaction of PET waste was investigated, 10 mol % of compound **1** performed the depolymerisation within 2 - 3 min at 190°C. The reaction led to the formation of the *bis*(2-hydroxyetil) tere-phtalamide (BHETA) monomer as it has been interpreted by ^{1}H-NMR spectroscopy. If ethylenediamine is used as depolymerization agent of PET waste, the efficiency of **1** is superior, complete conversion being achieved within 10 min with formation of *bis*(2-aminoethyl)tere-phthalamide (BAET) monomer as it has been established by ^{1}H-NMR spectroscopy.

Conclusions

Mechanistic investigations using NMR spectroscopy showed that TBD reacts with the ester to generate a covalently bonded adduct both at room temperature and in refluxing benzene [21]. Reaction of this compound with various glycols and amine derivatives revealed no acyl transfer, instead the reaction occurred at the carboxymethyl group of the covalently-bonded TBD adduct. Comparative investigations of the catalytic activity of **1** with its parent compound highlighted its superior efficiency for both glycolysis and aminolysis of PET wastes. In contrast to commercially available TBD which is very hygroscopic and suffers ageing upon exposure to carbon dioxide from air, this catalyst is considerably easy to handle. Further explorations of the catalytic potential of this amide-ester in the field of chemical depolymerization of PET wastes are ongoing in our research groups.

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