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Zinc titanate nanopowder: an advanced nanotechnology based recyclable heterogeneous catalyst for the one-pot selective synthesis of self-aggregated low-molecular mass acceptor–donor–acceptor–acceptor systems and acceptor–donor–acceptor triads[†]

Paramita Das,^a Ray J. Butcher^b and Chhanda Mukhopadhyay^{*a}

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Highly stable, environmentally benign ZnTiO₃ nanopowder has been prepared *via* a sustainable sol–gel method. The nanopowder (90 nm) has been thoroughly characterized by SEM, XRD, EDS, Laser Raman, photoluminescence, UV and IR. The activity of the catalyst was probed through one-pot four-component reaction of aldehydes, ketones and two equivalent propanedinitriles in water without requiring any additives or anhydrous conditions. The reaction requires two different catalytic functions, *i.e.*, an acidic one which is given by Ti(rv) ions and a basic one, given by the oxide ion incorporated within the ZnTiO₃ metal oxide framework. The advantages of this method lie in its simplicity, cost effectiveness, environmental friendliness, and easier scaling up for large scale synthesis without using high pressure, temperature and toxic chemicals. As water was used as a reaction medium and since we are particularly interested in the isolation of a non-aromatic intermediate, the elimination of poisonous HCN was prevented by the Lewis acid character of Ti⁴⁺ up to a sufficiently high temperature. Thus, this process can be considered as a "green" process. Elimination of HCN at higher temperatures still maintains "green" attributes as HCN can be trapped by the basic catalyst under such conditions. Spontaneous generation of low molecular mass self-aggregated organic materials, their one-dimensional packing, and interesting photophysical properties are reported.

Introduction

A "strong marriage" between nanotechnology and the principles and practices of green chemistry¹ holds the key to building an environmentally sustainable society. Nanotechnology offers us the opportunity to improve the green aspect of many processes and products. Organic low-dimensional nanostructures used as nanoscale building blocks have attracted considerable research interest in the development of novel nano-devices.² This interest is driven by the fact that organic nanostructures may exhibit a wide range of electrical, magnetic and optical properties which depend, sensitively, on both their shapes and sizes and thus, is likely to provide a new method for modifying the optical and electronic properties of organic functional materials.³ However, researchers continue to face great challenges in the construction of well-defined organic compounds that aggregate into larger molecular materials such as wires,^{3e} tubes,^{3f} rods, particles,^{3a-d} walls, films and other nanoscaled structural arrays. From this standpoint, an important challenge in the discovery of novel mesoscopic properties and the development of nanotechnology is to fabricate functional conjugated organic molecules with structural features that favor assembly into aggregate nanostructures with desired shape and size, *via* weak intermolecular interactions.

As catalysis lies at the heart of countless chemical protocols, another aspect of green chemistry to take into consideration is the development of green processes and pollution abatement catalysts. Recently, metal-based nanoparticles in the form of nanocatalysts have emerged as viable alternatives to conventional materials in various fields of chemistry, attracting interest among chemists. Metal-based nanoparticles are known to be promising materials for heterogeneous catalysis in a variety of organic transformations.⁴ In addition, metal-based nanoparticles have wide ranging applications in electronic, magnetic, optical, biological and mechanical materials because of their notable differences compared to bulk metals.⁵

2,6-Dicyanoanilines belong to typical acceptor–donor–acceptor (A–D–A) systems, which are the basis for artificial photosynthetic systems, materials possessing semiconducting or non-linear properties, and molecular electronic devices.⁶ Furthermore, 2,6-dicyanoanilines are useful intermediates for building blocks for cyclophanes to create a large molecular cavity and

^aDepartment of Chemistry, University of Calcutta, 92 APC Road, Kolkata-700009, India. E-mail: cmukhop@yahoo.co.in; Tel: +91-9433019610

^bDepartment of Chemistry, Howard University, Washington DC 20059, USA

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Scheme 1 $ZnTiO_3$ nanopowder catalyzed efficient synthesis of A–D–A triads and A–D–A–A systems under two different conditions.

host–guest complex.⁷ In addition, their biaryl unit is represented in several types of compounds of current interest including natural products, polymers, advanced materials, liquid crystals, ligands and medicinal compounds.^{7,8} Traditionally, the synthesis of 2,6-dicyanoanilines was catalyzed by a basic catalyst such as piperidine.⁹ Many homogeneous catalysts have also been employed for this condensation including NaOH,¹⁰ ethanediamine, and¹¹ Et₃N.¹² However, most of the reported methods are cumbersome, require prolonged reaction times,¹¹ have relatively poor yields, and involve the use of costly reagents¹³ and toxic solvents.¹⁴ Moreover, the main disadvantage of almost all the existing methods is that the catalysts are destroyed in the workup procedure and cannot be recovered or reused.^{10–14} On the other hand, no heterogeneous catalysts have been used for this transformation. Therefore, there is still a need for a simpler, more versatile, and environmentally friendly process.

Considering the above points and in continuation of our quest for developing green protocols for the synthesis of various products such as various nanoparticles, herein we employ ZnTiO₃ nanopowder as an efficient and heterogeneous catalyst for the synthesis of acceptor–donor–acceptor–acceptor (A–D–A–A) systems (4) as well as its aromatization product (A–D–A triads) (5) *via* a one-pot four-component reaction in aqueous media (Scheme 1).

Furthermore, the compound **4** is prone to aromatization by the elimination of hydrogen cyanide affording compound **5**. In some instances, the driving force of aromatization is so enhanced that the intermediate **4** cannot be isolated and the reaction affords only **5**.¹⁵ Yan *et al.* reported a multicomponent domino reaction of malononitrile, benzaldehyde and ethyl α -bromoacetate (or chloroacetonitrile) in refluxing acetonitrile, affording 2,6-dicyanoaniline (**5**) in 31–53% yields.¹⁶ However, only very few domino reactions are known for the synthesis of compound **4** with moderate yields.¹⁷ Therefore, we wish to disclose the development and implementation of a new method for one-pot selective generation of both the aromatic and non-aromatic intermediates under two different conditions.

Results and discussion

The synthesis of the nanostructured zinc titanate $(ZnTiO_3)$ (Scheme S1, see ESI[†]) in powder state has been carried out by a known method¹⁸ using zinc acetate [(CH₃COO₂)₂Zn], ethylene glycol (OHCH₂CH₂OH), titanium butoxide (C₁₆H₃₆O₄Ti) and citric acid anhydrous [C₃H₉(OH)(COOH)₃] (purity of the starting materials greater than 99.9%) (all in equimolar ratios). Even though the starting materials are not very sensitive to moisture, both the handling of chemicals and all procedures were carried out under a N₂ atmosphere.

Scanning electron microscopy (SEM) was used to study the morphology of the surface of ZnTiO₃ nanopowders calcinated at various temperatures: (A) 200 °C, (B) 500 °C and (C) 800 °C for 6 h (Fig. S2, see ESI†). The analysis of the obtained figure clearly shows that a higher calcination temperature favors particles with larger grain sizes (the grain size is about 90 nm for 800 °C, 70 nm for 500 °C and 35 nm for 200 °C) and higher density compared to a lower calcinated temperature because a higher temperature enhanced the atomic mobility and caused grain growth which resulted in better crystallinity. As shown in the SEM micrographs, the grain sizes seem to increase linearly with increasing calcination temperatures.

The exact crystal plane and the particle size were estimated by X-ray diffraction (XRD) analysis of the ZnTiO₃ nanopowder calcinated at 800 °C in air (Fig. S3, see ESI†). In the wide angle study, a characteristic peak—due to the crystal planes— appeared. The peaks correspond to the 220, 311, 400, 422, 511 and 440 planes of ZnTiO₃ which are consistent with the standard JCPDS reported values. Applying Sherrer's formula, $D_p = 0.941\lambda/\beta \cos \theta$ where D_p is the average grain size, λ is the X-ray wavelength equal to 1.5406 Å and β is the half-peak width, the particle sizes are found to be 91 nm. These results are in good accordance with the SEM observations.

The presence of Zn, Ti and O atoms was also observed in the EDX spectrum collected from SEM (Fig. S4, see ESI⁺).

Based on the SEM and XRD observations, the optical properties of the synthesized ZnTiO₃ nanopowder calcinated at 800 °C were investigated using Laser Raman and Photoluminescence measurements (Fig. S5, see ESI†). The Raman spectra of calcinated powder are in good agreement with the XRD pattern. The peaks located at about 139, 228, 351, 427, 445, 605 and 709 cm⁻¹ are ascribed to the perovskite structure of ZnTiO₃. These results agreed well with previous reports.¹⁹

The photoluminescence (PL) spectrum was acquired at r.t. with an excitation wavelength of 536 nm from 400 to 700 nm (Fig. S6, see ESI[†]). Room-temperature PL spectra of the ZnTiO₃ nanopowder show emissions in the visible light regions. It has been well understood that the deep level (DL) visible light emissions are due to various point defects.²⁰ From the position of the PL emission band at 536 nm, the optical gap can be calculated as 2.30 eV. PL depends on the degree of the system disordering, which leads to the appearance of new energy levels, both in the valence band and in the conduction band, decreasing the band gap. In the present case, a low temperature during synthesis increases the degree of disorder. As explained by Blasse and Grabmaier,²¹ the PL arises from a radiative return to the ground state, a phenomenon that is in concurrence with the non-radiative return to the ground state, in which the energy of the excited state is used to excite the vibrations of the host lattice, *i.e.* to heat the lattice. The radiative emission process occurs more easily if trapped holes or trapped electrons exist in the structure. The literature associated with the PL in titanates indicates that the

phenomenon is related to the presence of $[TiO_5]$ clusters, particularly from the local distortion of the Ti⁴⁺ ions within the TiO₆ octahedrons, oxygen vacancies, or charge transfers *via* intrinsic defects inside an oxygen octahedron²² leading to delocalized electron levels in the optical gap.

To further investigate the optical properties of ZnTiO₃ nanopowder, UV-vis absorption spectroscopy of the solid nanopowder catalyst was performed (Fig. S7, see ESI[†]). Fig. S7[†] shows absorbance maxima at 324 nm of ZnTiO₃ nanopowder calcinated at 800 °C. The band gap energy of ZnTiO₃ was calculated from the UV-vis absorption spectra which showed a strong absorption band (below 350 nm in wavelength) in the UV region. For the indirect band-gap semiconductor, the relation between the absorption edge and photon energy (hv) can be written as follows:

$$ahv = A(hv - E_g)^2$$

where α is the absorption coefficient, A is a constant, h is Planck's constant, v is the photon frequency and E_g is the optical band gap. The optical band gap for ZnTiO₃ nanopowder is about 3.78 eV, which is significantly larger than that reported for the bulk material (3.5 eV).²³ These results are in good accordance with the theoretical observations which suggested that the value of blue-shifting is inversely proportional to the square of the crystallite size due to the quantum confinement effect.²⁴ The band gap of 3.78 eV indicates that the cubic phase ZnTiO₃ is an indirect band gap semiconductor, which is consistent with that reported in the literature.²⁵

The nanopowder obtained by heating the catalyst at 800 °C exhibits a trace of absorption band probably due to δ (H₂O) around 1629 cm⁻¹, $v_{\rm S}$ (H₂O) ~ 3430 cm⁻¹ (Fig. S8, see ESI†). Absorption bands ~576 cm⁻¹ from ~400–800 cm⁻¹ can be ascribed to Ti–O stretching vibrations in ZnTiO₃. The broader absorption bands of the Ti–O stretching vibrations, as compared with those reported in ref. 26, may arise from the nanocrystalline nature of the sample.

From the XRD analysis (Fig. S3, see ESI[†]), ZnTiO₃ nanopowder was characterised by the cubic perovskite structure. Here O^{2^-} ions along with the larger cations (*i.e.* Zn²⁺) are in a *ccp* or *fcc* array and the smaller cations (Ti⁴⁺ ions) occupy the octahedral holes formed by the O²⁻ ions. Thus in the unit cell, 8 corners of a cube are occupied by Zn²⁺, at the centre of each face there is an O²⁻ ion, and at the centre of the cube, a Ti⁴⁺ ion is found. Thus, the contributions of the lattice points per unit cell are as follows: one Zn²⁺ (8 × 1/8 = 1, for corner point), three O²⁻ (6 × $\frac{1}{2}$ = 3, face centered point), one Ti⁴⁺ (1 × 1 = 1, for body centered point).²⁷ In this context we mention that ZnO adopts the hexagonal wurtzite structure and TiO₂ can exist in the anatase or rutile phase.²⁸

A short review on the literature depicts that BET surface area is a function of the Zn/Ti mole ratio. Mixed oxides have greater surface area, smaller particle sizes and higher generation of new catalytic active sites than the corresponding oxide homologues. This is extremely important since higher surface area favors adsorption of reaction molecules and small particle size is advantageous for minimal internal diffusion resistance of molecules thereby increasing the catalytic performance of heterogeneous catalysts.²⁹ Another advantage of using mixed oxides over simple addition of oxides is that while individual oxides have either acidic or basic properties, mixed oxides produce systems that have enhanced novel acidic as well as basic properties and by varying the mixing concentration, it is possible to control their acidic/basic active sites. For example, the basicity of the ZnO–TiO₂ system strongly depends on the ZnO content. Moreover, Bhattacharyya *et al.* reported that it is not the simple addition of ZnO and TiO₂ but rather, it is the ZnO–TiO₂ interface which is the source of catalytic activity.^{30a} This point was further supported by Gómez *et al.* who concluded that the interactions between the different crystalline structures coexisting in the mixed oxide should be responsible for observed activity and selectivity patterns.^{30b}

Transition metal oxides are extensively employed as catalysts because they possess an active centre which can adsorb reaction molecules. Chemical properties of the active sites can be adjusted by mixing an oxide catalyst with an oxide support, and so the interaction between the two metal catalysts is highly crucial for catalytic performance.²⁹ Therefore, these results strongly suggest that $ZnTiO_3$ materials have potential applications in catalytic fields.

To optimize the reaction conditions, a series of experiments were conducted with a representative reaction of 4'-methoxy acetophenone (1f) (2 mmol), 4-methoxy benzaldehyde (2a) (2 mmol) and malononitrile (3) (4 mmol), with variation of reaction parameters, such as catalyst, reaction temperature *etc.*, and the results are summarized in Table 1. Screening of the reaction

Table 1 Optimization of reaction conditions for the multicomponentcoupling reactions a



Entry	Catalyst (0.2 mmol)	Temp. (°C)	Time (h)	$\mathrm{Yield}^{b}(\%)$	
				4fa	5fa
1	NaOH	r.t. ^c	48	9	19
2	NaOH	60	6	0	45
3	NaOH	120	3	0	35
4	NaOAc	60	10	0	42
5	NaOAc/AcOH	60	10	20	25
6	Piperidine	60	12	12	43
7	Et ₃ N	60	13	18	40
8	Pyridine	60	15	22	39
9	MgO NPs	50	16	28	38
10	ZnO NPS	r.t. ^c	24	15	20
11	ZnO NPS	50	16	30	40
12	ZnO NPS	70	14	0	72
13	ZnO NPS/TiO ₂ NPs	r.t. ^c	4	79	0
14	ZnO NPS/TiO ₂ NPs	100	4	0	80
15	$ZnTiO_3 NPs^d$	r.t. ^c	3	93	0
16	ZnTiO ₃ NPs ^d	100	3	0	95
17	TiO ₂ NPs	50	15	0	0

^{*a*} All reactions were carried out in H₂O (2 mL) using the substrates according to the indicated ratio in mmol scale. ^{*b*} Isolated yields. ^{*c*} Here r.t. corresponds to 30 °C. ^{*d*} Thermally activated ZnTiO₃ at 800 °C in air.

conditions established that the nature of the catalyst and the temperature of the reaction medium had a significant effect on the yield of the non-aromatic product (4fa) and, consequently, the aromatic product (5fa).

It was found that 0.2 mmol of NaOH as the base catalyst could mainly isolate the aromatic compound (5fa) (19%) along with very small amount of non-aromatic compound (4fa) (9%) after 48 h stirring at room temperature (Table 1, entry 1). Repetition of the same experiment at 60 °C, yielded only the aromatic product (5fa) in 45% yield (Table 1, entry 2). This could probably be due to the ease of elimination of HCN at higher temperatures. The yield of 5fa decreased by up to 35% at a much higher temperature with NaOH (Table 1, entry 3). This was presumed to occur due to the competitive Cannizaro reaction,³¹ a typical reaction for aldehydes in basic media under high temperatures which yields an acid and consumes aldehyde in the reaction mixture. This was corroborated by the NMR spectra. Interestingly, with NaOH we always obtained the aromatic product (5fa) as the major product even at much lower temperatures. This is because NaOH promotes the elimination of the acidic component HCN. Therefore, we were in search of a catalytic system which carried out the reaction at room temperature to prevent the elimination of HCN so that the non-aromatic compound (4fa) could be isolated which would allow us to synthesize the aromatic compound (5fa) when needed. With NaOAc as a base catalyst, the reaction did not proceed at all at room temperature. However, increasing the temperature to 60 °C yielded only the aromatic product (5fa) in 42% yield (Table 1, entry 4). On the other hand, the use of NaOAc/AcOH as catalyst, showed a significant improvement in the yield of non-aromatic product (4fa) (20%) along with 25% of aromatic product (5fa) at 60 °C (Table 1, entry 5) indicating that the presence of an acid can prevent the elimination of the other acidic HCN which confirms our earlier observation-that the acid additive HOAc functioned to inhibit the elimination of another acidic component HCN very efficiently.¹¹ Thus, it was found that decreasing the base strength increases the yield of non-aromatic product (4fa) along with the overall yield (Table 1, entries 6-8) because of the lesser extent of HCN elimination with weaker base catalyst and also the lesser extent of the Cannizaro reaction of aldehydes. However, an improved yield was obtained with weaker bases like MgO and ZnO (Table 1, entries 9-12). Interestingly, we observed that TiO₂ was most effective in terms of prevention of elimination of another acidic component HCN in the presence of another strong Lewis acid Ti⁴⁺.³² Again MgO and ZnO nanoparticles were more effective than bulk MgO and ZnO in terms of reaction time and temperature. We also found that ZnO nanoparticles were potentially better catalysts than MgO nanoparticles. Therefore, the dual catalytic activity of ZnO NPs and TiO₂ NPs was essential for the room temperature synthesis of the non-aromatic compound (4fa) with a shorter reaction time (Table 1, entries 13, 14). The compounds obtained were highly pure as can be seen in the ¹H NMR spectra (see ESI [†]). Significant enhancement of the product yield and cleaner reaction conditions were the outcomes of this dual catalytic system. The decreased extent of the Cannizaro reaction and other side products formed under low temperatures and short reaction times could be a plausible reason. Therefore, from the entries 13-14 (Table 1) it is clear that selective generation of the non-aromatic compounds

4xy is only possible with Ti⁴⁺ since it can arrest the elimination of HCN. However, with other bases we have used, the aromatic compound 5xy is mostly formed even at r.t. Therefore, selective generation of the non-aromatic intermediate is not possible with other catalysts even if it is the desired product (Table 1, entries 10–12). Thus, the entries 10–14 (Table 1) clarify that Ti^{4+} has a definite role in the prevention of elimination of HCN, thus allowing the selective generation of non-aromatic 4xy and aromatic compounds 5xy at different temperatures. Therefore, ZnO/TiO₂ though it is a good catalyst for this reaction, leads to a yield that is not as high as that of ZnTiO₃ (Table 1, entries 15–16). Thus, ZnTiO₃ is the best catalyst for this particular reaction in generating non-aromatic and aromatic compounds. Moreover, when ZnO and TiO₂ were mechanically mixed in a 1:1 ratio then the elemental analysis of the recovered catalyst showed that the 1:1 ratio was not maintained after the first run. This may presumably be due to the loss of some amount of catalyst during filtration and therefore, it is unrealistic to expect that atom ratio would remain 1:1 after filtration. Table 1, entry 13 showed that the reaction with ZnO/TiO₂ afforded the 4fa in 79% yield and 100% selectivity. The elemental analysis of the recovered ZnO/TiO₂ showed that the atomic ratio was 1.0:0.8. When the same reaction was carried out with this recovered ZnO/TiO2, 8% of the aromatic product 5fa was formed along with 68% of non aromatic 4fa as is evident from the ¹H NMR spectra of the crude reaction mixture (see ESI [†]). This is due to the fact that TiO₂ cannot prevent the decomposition of 8% non aromatic 4fa in the presence of an excess of basic ZnO over TiO₂. These results firmly established that the 1:1 ratio must be maintained for the aforesaid selectivity and catalytic efficacy. To avoid the problem, mixed oxide ZnTiO₃ nanopowder was selected as the heterogeneous catalyst. After first run, this recycled catalyst was found to contain the same proportion of Zn and Ti as that of the original catalyst. The non aromatic product 4fa was selectively formed in 93% yield without the formation of 5fa at room temperature with ZnTiO₃ (Table 1, entry 15). Again the aromatic product 5fa was the only product at 100 °C (Table 1, entry 16). Starting materials were mostly unaffected with only TiO₂ as catalyst (Table 1, entry 17). Therefore, presence of ZnO as a base is necessary for this reaction to proceed. Thus, the efficacy and superiority of ZnTiO₃ with respect to other catalysts have been firmly established.

To analyze the temperature dependence on the yield of nonaromatic product (4fa) to the aromatic product (5fa), a series of experiments were conducted with a representative reaction of 4'methoxy acetophenone (1f) (2 mmol), 4-methoxy benzaldehyde (2a) (2 mmol), malononitrile (3) (4 mmol) and ZnTiO₃ nanopowder catalyst (0.2 mmol) in H₂O (2 mL) for 3 h at various temperatures with an interval of 10 °C (Fig. 1). Analysis of the reaction results established that whereas ZnTiO₃ can resist the elimination of HCN up to a sufficiently high temperature, ZnO alone could afford only a little of the non-aromatic compound (4fa) even at very low temperature. Again ZnO alone was not an efficient catalyst for the synthesis of aromatic compound (5fa) at room temperature. Therefore, ZnTiO₃ was the most efficient catalyst for room temperature synthesis of the non-aromatic compound (4fa), whereas the same catalyst afforded the aromatic compound (5fa) when heated to a sufficiently high temperature (~100 °C). However, elimination of the acidic component HCN



Fig. 1 Temperature dependence on the yield of non-aromatic product to the aromatic product.



Fig. 2 Yields at different catalyst loadings in the four-component coupling reaction of aldehydes, ketones and malononitrile.

at higher temperatures still maintains "greenness" as it can be trapped by the basic catalyst.

To determine the best amount of the catalyst, the synthesis of the non-aromatic product (4fa) was carried out in the presence of various amounts of catalyst in water at room temperature. Fig. 2 shows a remarkable increase in output according to the increase in the quantity of the catalyst up to 0.2 mmol. With a higher amount of catalyst no significant increase in the yield was observed. In order to use the minimum amount of the catalyst, we have been limited to 0.2 mmol for the continuation of the study.

With these optimized conditions in hand, this multicomponent reaction can be readily diversified through a combination of a range of ketones, aldehydes and malononitrile to synthesize the non-aromatic products (4) as well as aromatic products (5) under two different conditions and the results obtained are summarized in Schemes 2 and 3 respectively. Among the ketones, alicyclic as well as aromatic ketones afforded excellent yields (Scheme 2,



Scheme 2 Activated ZnTiO₃ nanopowder catalysed one-pot synthesis of non-aromatized product at r.t.

4aa–fa and Scheme 3, **5ac–gm**). A variety of aromatic ketones with electron-withdrawing as well as electron-donating groups on the aromatic ring were converted into desired products in good to excellent yields. In addition, the use of aliphatic ketones was also examined (Scheme 2, **4hm** and Scheme 3, **5hm**). It is



Scheme 3 Activated ZnTiO₃ nanopowder catalysed one-pot synthesis of aromatized product at 100 °C.

important to mention that the selectivity of this reaction towards CH₃CO- rather than RCH₂CO- $[R = CH (CH_3)_2]$ observed in the case of products 4hm and 5hm (Schemes 2 and 3 respectively) probably resulted from the instability of the carbanion (7h) because of the electron donating inductive effect of the



Fig. 3 (a) Instability of the carbanion in 7h. (b) Generation of carbanion in RCOCH₂R'.



Fig. 4 Difference in the structure of all the non-aromatic compounds derived from alicyclic ketones from all the previous reported structures.

alkyl group (Fig. 3(a)).³³ However, when R = Ph in $RCOCH_2R'$ then irrespective of the electron-donating $(R' = CH_3)$ or electrowithdrawing nature of the R' group (R' = Ph) there is no second choice of generation of carbanion except for 7 [Fig. 3(b)]. Therefore, irrespective of the steric crowding among the substituents, fully substituted products were also isolated in good to excellent vields (Scheme 2, 4ie-jm and Scheme 3, 5io). To further expand the scope of the reaction the use of heteroaryl methyl ketones was investigated (Scheme 3). 2-Acetylthiophene was easily transformed into the desired products in excellent yields (Scheme 3, 5kb and 5kk).

Despite the difficulty of a Knoevenagel condensation reaction with electron-rich carbonyl, the reaction occurred successfully with 4-methoxy benzaldehyde, 3,4-dimethoxy benzaldehyde, 2,5-dimethoxy benzaldehyde, 2,5-dimethyl benzaldehyde and 4methyl benzaldehyde (Scheme 2, 4aa-ab, 4ba-bb, 4bh-fa, 4ie, 4je and Scheme 3, 5ac-5ad, 5bh-cb, 5fa, 5kb). To check the generality of the reaction, aldehydes with electron-withdrawing substituents on the aromatic ring were also employed (Scheme 2, 4ag-ao, 4bk-hm, 4ih-im, 4jm and Scheme 3, 5af-bk, 5cmem, 5gm-io, 5kk). In addition, the use of aliphatic aldehydes was also examined (Scheme 2, 4bh and Scheme 3, 5bh). To further expand the scope of the reaction, the use of heteroaryl aldehyde was investigated. Pyridine-4-aldehyde was easily transformed into the desired products in excellent yields (Scheme 2, 4ao and Scheme 3, 5io).

Again, the novelty of our reaction lies in the fact that all the non-aromatic compounds (4) derived from alicyclic ketones (Fig. 4a) have a slightly different structure from all the previously reported structures (12) (Fig. 4b).¹¹ We have confirmed our supposition unambiguously by X-ray crystallographic analysis of compound 2-amino-4-(3-nitro-phenyl)-5,6,7,8-tetrahydro-4H-naphthalene-1,3,3-tricarbonitrile (4aj) (CCDC 836803) (Fig. 5) and compound 2-amino-6-(2,5-dimethoxy-phenyl)-5-



Fig. 5 ORTEP representation of **4aj** showing the crystallographic numbering (CCDC 836803).



Fig. 6 ORTEP representation of **5cb** showing the crystallographic numbering (CCDC 812619).

methyl-4-phenyl-cyclohexa-2,4-diene-1,1,3-tricarbonitrile (4ie) (Fig. S9, see ESI[†]). The final structure of the aromatic compound was confirmed by the X-ray crystallographic analysis of compound 2-amino-4-*p*-tolyl-6,7,8,9-tetrahydro-5*H*-benzocycloheptene-1,3-dicarbonitrile (5cb) (CCDC 812619) (Fig. 6) and compound 3-amino-6-methyl-5-pyridin-4-yl-biphenyl-2,4-dicarbonitrile (5io) (Fig. S10, see ESI[†]).

A plausible mechanism for the formation of 2,6-dicyano anilines catalyzed by ZnTiO₃ nanopowder is shown in Scheme 4. The reaction commences with the formation of the Knoevenagel condensation product from aldehyde with malononitrile.34 This is evident from the NMR spectrum of the major product (6, see ESI †), isolated after few minutes in the reaction of 4'-methoxy acetophenone (1f) (2 mmol), 4-methoxy benzaldehyde (2a) (2 mmol), malononitrile (3) (4 mmol). This intermediate (6) undergoes a Mannich-type reaction with another molecule of ketone (1), and subsequent elimination of the malononitrile leads to the intermediate (9). The structure of 9 is confirmed from the NMR spectrum of the major product (9, see ESI †), isolated by quenching the reaction after 45 min. Again the attack of malononitrile on intermediate (9), yields intermediate (10). This is evident from the NMR spectrum of the major product isolated after 1.30 h (see ESI [†]). Finally, the ring is produced by the attack of second molecule of malononitrile on the intermediate (10) followed by the elimination of HCN.

Here, oxides of the $ZnTiO_3$ metal oxide framework acting as a base and Ti^{4+} coordinate with the carbonyl oxygen, thus



Scheme 4 A plausible mechanistic pathway to explain the ZnTiO₃ nanopowder catalyzed formation of 2,6-dicyanoanilines.

increasing the electrophilicity of the carbonyl carbon and thereby making it possible to carry out the reaction at room temperature and at short reaction time. Obviously the acid character of Ti⁴⁺ in the reaction functioned to efficiently inhibit the elimination of HCN up to a sufficiently high temperature.³²

Here, despite Knoevenagel condensation being a net dehydration of the water molecule, the reaction is favored in aqueous medium. A plausible explanation is that water forms several hydrogen bonds with the catalyst and the organic molecule, thereby acting as a bridge between the homogeneous and heterogeneous phases.³⁵ Thus, realizing the environmental concerns,³⁶ as well as the vast utility and scope of reactions^{36a,37} carried out in water, we established water to be the preferred solvent.

In order to validate the recyclability of the current $ZnTiO_3$ nanopowder catalyst, the re-use investigation was performed in a model reaction of 4'-methoxy acetophenone (**1f**) (2 mmol), 4-methoxy benzaldehyde (**2a**) (2 mmol), malononitrile (**3**) (4 mmol) and $ZnTiO_3$ nanopowder catalyst (0.2 mmol) in H₂O (2 mL) for 3 h at r.t. producing **4fa** (Table 2).

Another recycling experiment on producing 5fa was carried out and it was found that the catalyst had the potential of efficient recycling for at least 6 cycles without any loss of catalytic activity. For this purpose, a model reaction of 4'-methoxy acetophenone (1f) (2 mmol), 4-methoxy benzaldehyde (2a)

Table 2 Reusability studies of $ZnTiO_3$ nanopowder catalyst for the synthesis of 4fa



^a Reaction was carried out with recovered catalyst. ^b Isolated yields.

Table 3 Reusability studies of ${\rm ZnTiO}_3$ nanopowder catalyst for the synthesis of 5fa



(2 mmol), malononitrile (3) (4 mmol) and ZnTiO₃ nanopowder catalyst (0.2 mmol) in H_2O (2 mL) for 3 h at 100 °C was carried out and the results are represented in Table 3.

Nearly quantitative catalyst (up to 98%) could be recovered from each run. In a test of six cycles, the catalyst could be reused without significant loss of catalytic activity. The slight reduction in yield is probably due to the loss of some catalyst at the time of filtration. The recovered catalyst after six runs had no obvious change in structure according to the FT-IR spectrum in comparison with the fresh catalyst (Fig. S8, see ESI†). The XRD observation of the recovered catalyst was also made and there was no obvious change in morphology (Fig. S3, see ESI†). These results revealed that the catalyst was very stable and could induce these conditions.



Fig. 7 SEM image of the nanostructured materials of compound 4ba.

Design and easy access to the low molecular mass self-aggregated organic materials (LMSOM) is now a new challenge in organic synthesis, wherein macrocyclic compounds or optically insensitive alkyl chain/steroidal groups substituted compounds have usually been utilized for the fabrication of 1D organic nanomaterials.^{38,39} In this regard, the generation of novel selfaggregated architectures of well-defined shape and size from 2,6dicyanoanilines is important. In a bid to our continuous effort to design and synthesize significant, diverse, complex and medicinally important organic frameworks and to study their self-assembly properties, we herein report a new class of LMSOM from **4ba** and **5bk** (Schemes 2 and 3 respectively) which are easily accessible by the one-pot green synthesis protocol.

However, these small organic molecules spontaneously form tunable nanomaterials in common organic solvents. To gain an insight into the aggregation morphology of the nanomaterials formed by compound **4ba**, two different solvents have been subjected to SEM. In THF it forms organic materials of spherical dimension with a "Kadam flower-like" well-defined shape constructed by highly self-aggregated nanosheets about 350 nm in width (panels a–c, Fig. 7), whereas tube-like nanomaterials are obtained in chloroform at about 70 nm in width (panels d–e, Fig. 7). However, an insight into the aggregation morphology formed by compound **5bk** in chloroform, gave flower-like welldefined shape with each petal about 100 nm in width (panels a–b, Fig. 8).

The flaky structure of compound **5kb** was further confirmed from the atomic force microscopy (AFM) analysis in chloroform (panel c, Fig. 8) where the aspect ratio was found to be 2.2353. Fig. 8(d) shows the 3D view of the compound in chloroform.

It is interesting for us to screen the polysubstituted 2,6-dicyanoanilines for their optical properties. The correlation between



Fig. 8 SEM and AFM images of the LMSOM of compounds 5bk.

optical properties and the molecular structure can be described only empirically, since no detailed theoretical predictions are possible.⁴⁰ A large number of compounds in a combinatorial library should correlate to a better understanding of the inherent structure-property relationships from which specifically tailored materials can be produced. From the library, two members 4ba and 5bk with the most intensive fluorescence were selected. The large red shift in UV, measured in the self-aggregated solid state of compound 5bk compared to their dilute solutions in three different solvents is probably due to the J-aggregation of the compound leading to the formation of the highly-ordered stacklike architecture (panels a, b, Fig. 9). Similar observations were found in UV spectra of compound 4ba with an additional vibrational hump existing around 300 nm in EtOAc and THF compared to that in CHCl₃ (Fig. S11 and S12 see ESI⁺). The spectral properties of compounds 4ba and 5bk are further emphasized in the fluorescence study. Maximum wavelengths $(\lambda_{\rm em} = 403-423 \text{ nm})$ were observed for compound **5bk** in CHCl₃, EtOAc and THF. The bathochromic shift observed for the emission spectra of compound 5bk in EtOAc and THF compared to that in CHCl₃ is attributed to the stronger hydrogenbonding with the NH₂ group of compound **5bk** with the oxygen atoms of the solvents leading to the stabilization of the excited state, thereby decreasing the energy gap and increasing the emission wavelength (panel c, Fig. 9). Unusual fluorescence amplification is also observed in both dilute and higher concentrations. The planar aromatic molecules with strong assembly properties exhibited amplified fluorescent sensing ability because of growing unidirectional π - π stacking (panel d, Fig. 9). Similar fluorescence amplification was also observed with compound 4ba. The additional emission wavelength of the compound 4ba



Fig. 9 Optical properties (UV and fluorescence) of the compound 5bk.

in EtOAc and THF compared to that in CHCl₃ is probably due to the structured vibrational spectra (Fig. S13, see ESI⁺).

In view of possible applications of these compounds (*e.g.*, as organic light-emitting diodes) the NH₂ substituted A–D–A and A–D–A–A systems are of interest since these compounds can be transformed into more thermostable derivatives through their amino groups. Also, the subsequent step of the combinatorial development process, namely structural optimization should be possible. The application of combinatorial strategies for screening and optimization of organic charge-transporting materials in a spatially addressable library of organic light-emitting diodes was reported by Schmidt *et al.*⁴¹

Conclusions

In conclusion, zinc titanate nanopowder has been synthesized and characterized using an array of sophisticated analytical techniques. It is demonstrated that such ZnTiO₃ nanopowder performs efficiently as a recyclable heterogeneous catalytic system for the one-pot construction of diverse one donor and poly acceptor systems containing a 2,6-dicyanoaniline moiety involving four-component condensation of aldehyde, ketone and two equivalent malononitrile in aqueous media. We have found Ti⁴⁺ as an active component for the catalytic process. This versatile approach provides direct access to the non-aromatic intermediate containing one donor and three acceptors, thus preventing the elimination of HCN. The key findings of high significance described in this work are three-fold. The first one is that ZnTiO₃ catalytic system enables "sensitive substances" such as pyridine-4-aldehyde, 2-acetyl thiophene, highly activated aromatic aldehydes (containing -NO₂ groups), aliphatic ketones such as isobutyl methyl ketones and aliphatic aldehydes such as butyraldehyde to react under our experimental condition to obtain corresponding 2,6-dicyanoamines in good to excellent yields. The second key finding in our work is that all the nonaromatic compounds derived from alicyclic ketones have slightly different structures from all the previously reported structures. The third finding in our work is that no anhydrous conditions are needed to promote the reaction and a reasonably low amount of ZnTiO₃ nanocatalyst is sufficient enough to catalyze our reaction. In addition, the route takes advantages of the abundance of aldehydes and ketones available commercially to make 2,6-dicyanoamines. These key findings make the nanotechnology based heterogeneous catalysis platform provided herein inherently advanced, economical, green and therefore, environmentally sustainable for the one-pot synthesis of 2,6-dicyanoamines. Using this robust green protocol we have synthesized UV and fluorescent active LMSOM forming tunable 1D stacking suitable for designing biosensors and optoelectronic nanodevices.

Experimental

Synthesis of ZnTiO₃ nanopowder catalyst

The ZnTiO₃ powders were prepared by sol–gel method using zinc acetate [(CH₃CO₂)₂Zn], ethylene glycol (HOCH₂CH₂OH), titanium butoxide (C₁₆H₃₆O₄Ti) and citric acid anhydrous [C₃H₄(OH)(COOH)₃] (purity of the starting materials greater

than 99.9%). Even though the starting materials are not very sensitive to moisture, both the handling of chemicals and procedures were carried out under a N_2 atmosphere. Equimolar zinc acetate and titanium butoxide are separately dissolved in deionized water and ethanol and mixed in a two-neck round bottom flask. When the precursor was completely dissolved in the solution, equimolar amounts of citric acid and ethylene glycol were added. Ethylene glycol (propionic acid) is added to the above as a stabilizing agent. The contents are refluxed in N_2 atmosphere for 2 h at 25 °C, yielding a homogeneous organic solution. After refluxing, the contents are double filtered to dispose of any small particles which may be present from the mixing of the materials. Obtained powders were heat treated from 200 °C to 800 °C in air, respectively.

General procedure for the synthesis of non-aromatic intermediate A–D–A–A system (4aa–4jm)

Ketone 1 (2 mmol), aldehyde 2 (2 mmol), malononitrile 3 (4 mmol) and 0.2 mmol of activated ZnTiO₃ nanopowder catalyst were added to 2 mL water and the reaction mixture was stirred at r.t. for 3 h. After completion of the reactions (monitored by disappearance of the starting material in the thin layer chromatography), ethyl acetate (5 mL) was added to the whole reaction mixture and the solid catalyst was separated from the mixture by filtering through a sinter funnel. The recovered catalyst was washed several times with water and acetone, dried in a desiccator and stored for another consecutive reaction run. Pure organic compounds were afforded by evaporation of the solvent in a rotary evaporator and the residue was subjected to silica gel (60-120 mesh) column chromatography using ethylacetatepetroleum ether as eluents. The products were characterized by standard analytical techniques such as ¹H NMR, ¹³C NMR, FTIR, elemental analysis, melting point determination, X-ray crystallographic analysis and all gave satisfactory results (see ESI[†]).

General experimental procedure for the synthesis of 2,6dicyanoanilines (A–D–A triads) catalyzed by ZnTiO₃ nanopowder (5ac–5kk)

A mixture of ketone 1 (2 mmol), aldehyde 2 (2 mmol), malononitrile 3 (4 mmol) and activated ZnTiO₃ nanopowder catalyst (0.2 mmol) in water (2 mL) was heated under reflux at 100 °C for 3 h. After completion of the reactions (monitored by disappearance of the starting material in the thin layer chromatography), ethyl acetate (5 mL) was added to the whole reaction mixture and the solid catalyst was separated from the mixture by filtering through a sinter funnel. The recovered catalyst was washed several times with hot water and acetone, dried at 300 °C for 4 h and stored in a desiccator for another consecutive reaction run. Pure organic compounds were afforded by evaporation of the solvent in a rotary evaporator and the residue was subjected to silica gel (60-120 mesh) column chromatography using ethylacetate-petroleum ether as eluents. The products were characterized by standard analytical techniques such as ¹H NMR, ¹³C NMR, FTIR, elemental analysis, melting point determination, X-ray crystallographic analysis and all gave satisfactory results (see ESI[†]).

Experimental procedure for preparation of intermediate 6

Ketone 1 (2 mmol), aldehyde 2 (2 mmol), malononitrile 3 (4 mmol) and 0.2 mmol of activated $ZnTiO_3$ nanopowder catalyst were added to 2 mL water and the reaction mixture was stirred at r.t. for 5 min. To the reaction mixture, ethyl acetate (5 mL) was added and the solid catalyst was separated from the mixture by filtering through sinter funnel. The solvents were evaporated in rotary evaporator and the residue was subjected to silica gel (60–120 mesh) column chromatography using ethylacetate–petroleum ether as eluents to give Knoevenagel product 6 (357 mg, 97%) as a light yellow solid.

Experimental procedure for preparation of intermediate 9

Ketone 1 (2 mmol), aldehyde 2 (2 mmol), malononitrile 3 (4 mmol) and 0.2 mmol of activated $ZnTiO_3$ nanopowder catalyst were added to 2 mL water and the reaction mixture was stirred at r.t. for 45 min. To the reaction mixture, ethyl acetate (5 mL) was added and the solid catalyst was separated from the mixture by filtering through sinter funnel. The solvents were evaporated in rotary evaporator and the residue was subjected to silica gel (60–120 mesh) column chromatography using ethylacetate–petroleum ether as eluents to give Aldol product 9 (515 mg, 96%) as a white solid.

Experimental procedure for preparation of intermediate 10

Ketone 1 (2 mmol), aldehyde 2 (2 mmol), malononitrile 3 (4 mmol) and 0.2 mmol of activated $ZnTiO_3$ nanopowder catalyst were added to 2 mL water and the reaction mixture was stirred at r.t. for 1.30 h. To the reaction mixture, ethyl acetate (5 mL) was added and the solid catalyst was separated from the mixture by filtering through sinter funnel. The solvents were evaporated in rotary evaporator and the residue was subjected to silica gel (60–120 mesh) column chromatography using ethylacetate–petroleum ether as eluents to give intermediate 10 (607 mg, 96%) as a yellow solid.

General procedure for the synthesis of non-aromatic intermediate and aromatic compound catalyzed by ZnO nanopowder (Table 1, entry 10)

4'-Methoxy acetophenone **1f** (2 mmol), 4-methoxy benzaldehyde **2a** (2 mmol), malononitrile **3** (4 mmol) and 0.2 mmol of ZnO nanopowder catalyst were added to 2 mL water and the reaction mixture was stirred at r.t. for 24 h. After completion of the reaction two spots—one of aromatic product **4fa** and the other of non-aromatic compound **5fa**—were monitored in the thin layer chromatography. Ethyl acetate (5 mL) was added to the whole reaction mixture and the solid catalyst was separated from the mixture by filtering through a sinter funnel. Pure organic compounds were afforded by evaporation of the solvent in a rotary evaporator and the residue was subjected to silica gel (60–120 mesh) column chromatography using ethylacetate– petroleum ether as eluents. The products were characterized by standard analytical techniques such as ¹H NMR, ¹³C NMR, FTIR, elemental analysis, melting point determination and all gave satisfactory results. All the other entries incorporated in Table 1 have been performed in a similar fashion.

Detailed experimental procedure to confirm the presence of Ti^{4+} in ZnTiO₃ prevents the formation of HCN at r.t. (Table 1, entry 15)

4'-Methoxy acetophenone **1f** (2 mmol), 4-methoxy benzaldehyde **2a** (2 mmol), malononitrile **3** (4 mmol) and 0.2 mmol of activated ZnTiO₃ nanopowder catalyst were added to 2 mL water and the reaction mixture was stirred at r.t. for 3 h. After completion of the reactions (monitored by disappearance of the starting material in the thin layer chromatography), the crude reaction mixture was filtered and washed 10 times with hot water. To the combined filtrate several drops of AgNO₃ was added. No white precipitate of AgCN was obtained indicating no cyanide in the medium. Moreover when the same reaction was carried out in presence of other catalysts, the above test was positive. Thus, from the above test we can confirm that the presence of Ti⁴⁺ in ZnTiO₃ prevents the elimination of HCN at r.t.

Detailed experimental procedure to confirm the formation of HCN at 100 °C (Table 1, entry 16) and reusability of the catalyst

A mixture of 4'-methoxy acetophenone 1f (2 mmol), 4-methoxy benzaldehyde 2a (2 mmol), malononitrile 3 (4 mmol) and activated ZnTiO₃ nanopowder catalyst (0.2 mmol) in water (2 mL) were heated under reflux at 100 °C for 3 h. After completion of the reactions (monitored by disappearance of the starting material in the thin layer chromatography), the crude reaction mixture was just filtered and to the filtrate several drops of AgNO₃ was added. No white precipitate of AgCN was obtained indicating no cyanide in the medium. However, after thorough washing the crude mixture (contained both ZnTiO₃ and the aromatic product) 10 times with hot water when 2 drops of AgNO₃ was added to the combined filtrate a white precipitate of AgCN was obtained. The foregoing results established that the CN⁻ in the medium came from the trapped HCN which is adsorbed inside the nano-pores of ZnTiO₃ and did not occupy lattice sites or interstitial position or covalently bonded with either Ti⁴⁺ or Zn^{2+} which would otherwise result in the shifting of the original peaks not observed in the XRD pattern. After further heating the ZnTiO₃ to 300 °C for 4 h any residual HCN was removed. The water extract after further washing the catalyst did not contain any trace of CN⁻. The recovered catalyst was stored in a desiccator for another consecutive reaction run.

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