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Synthesis, Photophysical and Electrochemical Properties of Donor-Acceptor Type Hydrazinyl Thiazolyl Coumarins

G. Kumar, ^a G. Trivikram Reddy,^a B. Ramakrishna,^b Y.V. Divyasri,^a L. Subramanyam Sarma^a and N. C. Gangi Reddy*a

A water mediated MCR strategy has been developed for the synthesis of donor (D)-acceptor(A) type hydrazinyl thiazolyl coumarins (HTCs) (4) in excellent isolated yields (90-98%) from a three component reaction of aromatic aldehydes/ketones (1), thiosemicarbazide (2) and 3-(2-bromoacetyl)-2H-chromen-2-one (3) catalyzed by an environmentally compatible montmorillonite (MMT) K10 clay at RT for 20-40 min. The present MCR has several advantages which include its wide-spread substrate scope, eco-compatibility, short reaction times and the products does not require chromatographic purification. Besides, the method is simple to perform, easy to construct C-N, C=N and C-S bonds in one-pot and can be scaled up to a gram level. Moreover, the catalyst is reused for 7 times without significant change of activity. Photo physical properties of the synthesized D-A type HTCs are also studied and noticed that the fluorescence properties are varied with the position of electron donating group on the aromatic ring of aldehyde/ketone of HTCs. Most of the compounds exhibited bright fluorescence in chloroform (1.0 × 10⁻⁵ M) with emission maxima ranging from 409 to 511 nm and large Stokes shifts. Further, The HOMO and LUMO energy levels of HTCs are found in the range from -5.65 eV to -5.22 eV and -2.67 eV to -2.17 eV, respectively and in good agreement with the reported hole transporting materials.

Introduction

Design and development of multi-component reactions (MCRs) in water have received considerable attention, particularly in the areas of organic synthesis, combinatorial synthesis, drug discovery, agrochemistry and material science.¹⁻³ Water is universally accepted benign solvent for synthetic organic chemistry, because of its natural abundance, non-toxicity, large dielectric constant, high heat capacity, cost-efficiency, non-flammability, extensive hydrogen bonding, environmental compatibility etc.3a-d Further, the search and identification of water-compatible catalysts for MCRs is one of the most active areas of research in organic synthesis.³

Fluorescent heterocyclic compounds are an important class of organic materials and received great attention because of their wide variety of applications in the fields of organic electronics and biomedical research.⁴ Therefore, the design and development of donor-acceptor type fluorescent heterocyclic molecules by incorporating both hole-transport and electrontransport units is one of the continuing objectives in the

Hyderabad 500 046, India.

current reseach.⁵ Among the heterocycles, coumarins and thiazoles are considered as privileged heterocyclic compounds because of their potential optoelectronic and biological properties.⁶⁻⁹ In particular, the hydrazinyl thiazolyl coumarin (HTC) derivatives exhibit promising biological activities which includes antimicrobial, antioxidant, antibacterial, antitubercular, antitumor activities etc.¹⁰ Till now, both two step and one-pot synthetic protocols are available for the synthesis of HTCs. The reported two-step methods proceed through the formation of thiosemicabazone by the reaction of carbonyl compounds with thiosemicarbazide followed by cyclization with 3-bromoacetylcoumarin.^{10a-d,i,j} However, the major margins of the reported methods are the involvement of multiple steps, use of expensive techniques and are unsuitable for large-scale applications. Furthermore, these protocols have narrow substrate scope, procedural complexity and lengthy reaction times. To date, very limited one-pot methods have been reported for the synthesis of hydrazinyl thiazolyl coumarins from ketones, thiosemicarbazide and phenacyl 3-(2-bromoacetyl)-2H-chromen-2-ones.^{10k,l} bromides or Though the reported one-pot methods are able to provide the desired products, but there are still some drawbacks like the usage of acetic acid as catalyst under harsh reaction conditions, lengthy reaction times, (Ibrar et al.,),^{10k} limited substrate scope (Rao et al., applied the method only on three liquid alicyclic ketones)¹⁰¹ and lack of gram scale feasibility. To overcome the aforesaid shortcomings, the development of facile, scalable, green and sustainable MCR strategy is still required for the synthesis of pharmacologically important

^{a.} Department of Chemistry, School of Physical Sciences, Yogi Vemana University,

Kadapa - 516 003, Andhra Pradesh, India.

^{b.} School of Chemistry, University of Hyderabad, Central University P.O.,

E-mail: ncgreddy@yogivemanauniversity.ac.in

Electronic Supplementary Information (ESI) available: [General Experimental, Characterization data, copies of ¹H NMR, HRMS and MS spectra of title compounds and crystallographic data of 4b in CIF format (CCDC 1952520). 58 See DOI: 10.1039/x0xx00000x

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59 60 HTCs. Moreover, no examples of fluorescent HTC compounds have been reported so far.

In the present paper, we describe a practical and green MCR strategy for the synthesis of HTC (4) derivatives *via* a threecomponent reaction of aromatic aldehydes/ketones (1), thiosemicarbazide (2) and 3-bromoacetylcoumarin in the presence of montmorillonite (MMT) K10 clay¹¹ as a water compatible and reusable heterogeneous green solid acid catalyst under ambient reaction conditions (Scheme 1). Further, the photophysical and electrochemical properties of the synthesized donor (D) - acceptor (A) type HTC compounds were studied.



Scheme 1. MMT K10 clay catalyzed multi-component synthesis of diversified HTC derivatives (4a-4ak) in water.

Results and discussion

In the present study, we aimed to (i) develop a watermediated 3-component reaction for the synthesis of HTCs by incorporation of three important pharmacophores i.e. coumarin, thiazole and imine group in a single step operation ii) identify the water-compatible, environmentally benign and reusable catalyst for the above 3-component reaction iii) apply the optimized method for the synthesis of a series of HTCs and iv) study the photophysical and electrochemical properties of the synthesized D-A type HTCs. To achieve the targets, initially, a control experiment was conducted for the 3-component synthesis of (E)-3-(2-(2-benzylidenehydrazinyl)thiazol-4-yl)-2Hchromen-2-one (4a) by using benzaldehyde (1a), thiosemicarbazide (2) and 3-(2-bromoacetyl)-2H-chromen-2one (3) as model substrates. Unfortunately, no product was formed in the absence of catalyst in water at RT (Table 1, entry 1). Further, the same reaction was repeated by employing a variety of Lewis acid catalysts such as AlCl₃, FeCl₃, TiCl₄, ZnCl₂, SnCl₄, ZrOCl₂, MMT K10 clay, Sc(OTf)₃ and Yb(OTf)₃ in various solvents at RT (Table 1, entries 2-10). After examining these catalysts and solvents, it was found that the MMT K10 clay (2.5 wt %) in water was the best option to obtain better yield (75%) of the product (4a) (entry 8, Table 1) whereas the other catalysts afforded moderate to low yields of 4a (entries 2-7, 9 & 10, Table 1). From this study, it was also observed that the 3-component reaction proceeded well in polar protic solvents as compared with polar aprotic solvents (Table 1). Further, the amount of MMT K10 clay was varied (5.0, 7.5, 10.0, 12.5, 15.0, 17.5 and 20.0 wt%) to improve the yield of 4a (Table 2). The study revealed that the 12.5 wt % of MMT K10 clay was the best option to get the highest yield of product 4a (98%) in water at RT within a short reaction time (20 min) (Table 2, entry 5). Further, it was also found that the same yields were obtained despite the increase in the amount of loading of catalyst i.e. 15.0, 17.5 and 20.0 wt% (Table 2, entries 6-8).

 Table 1. Optimization of reaction conditions for the synthesis of (E)-3-(2-(2-benzylidenehydrazinyl)thiaz@P4101)22A428Home82E

 2-one (4a).^a



Entry	Catalysts	Solvent	Time	Product	Yield⁵
	(2.5 wt-%)		(min)		(%)
1 ^c	-	H ₂ O	180	4a	-
		H ₂ O	60		30
2		EtOH	60		35
2	AICI ₃	Isopropanol	60	4a	30
		EtOAc	60		-
		Acetonitrile	60		5
		H ₂ O	60		25
2		EtOH	60		20
5	FeCl ₃	Isopropanol	60	4a	20
		EtOAc	60		-
		Acetonitrile	60		10
		H ₂ O	60		35
4		EtOH	60		25
4	TiCl ₄	Isopropanol	60	4a	20
		EtOAc	60		-
		Acetonitrile	60		5
		H ₂ O	60		30
-		EtOH	60		30
5	ZnCl ₂	Isopropanol	60	4a	25
		EtOAc	60		-
		Acetonitrile	60		10
		H ₂ O	60		25
6		EtOH	60		20
		Isopropanol	60		20
	$SnCl_4$	EtOAc	60	4a	-
		Acetonitrile	60		-
		H ₂ O	60		40
7		EtOH	60		35
/	ZrOCl ₂	Isopropanol	60	4a	40
		EtOAc	60		-
		Acetonitrile	60		10
		H ₂ O	60		75
Q	MMT K10	EtOH	60		65
0	clay	Isopropanol	60	4a	55
		EtOAc	60		-
		Acetonitrile	60		15
		H ₂ O	60		55
٩		EtOH	60		60
5	Sc(OTf)₃	Isopropanol	60		55
		EtOAc	60	4a	-
		Acetonitrile	60		20
		H ₂ O	60		60
10		EtOH	60		65
10	Yb(OTf)₃	Isopropanol	60	4a	50
		EtOAc	60		-
		Acetonitrile	60		20

^a**Reagents and conditions:** Benzaldehyde (1a) (10.0 mmol), thiosemicarbazide (2) (10.0 mmol), 3-(2-bromoacetyl)-2H-chromen-2-one (3a) (10.0 mmol), catalyst (2.5 wt-%) in various solvents at room temperature; ^bIsolated yield. ^cReaction did not proceed in the absence of catalyst.

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 Table 2. Screening of catalyst loading for the betterment of yield of (4a).^a

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	Entry	MMT K10 clay	/ Solvent	Time Product		Yield ^b			
		(wt-%)		(min)		(%)			
	1	2.5	H ₂ O	60	4a	75			
	2 5.0		H ₂ O	60	4a	83			
	3	7.5	H ₂ O	40	4a	88			
	4	10.0	H ₂ O	40	4a	92			
	5	12.5	H ₂ O	20	4a	98			
	6	15.0	H ₂ O	20	4a	98			
	7	17.5	H ₂ O	20	4a	98			
	8	20.0	H ₂ O	20	4a	98			
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^aReagents and conditions: Benzaldehyde(1a) (10.0 mmol), thiosemicarbazide (2) (10.0 mmol), 3-(2-bromoacetyl)-2H-chromen-2one (3a)(10.0 mmol), MMT K10 clay (2.5% to 20.0 wt-%) in water at room temperature; ^bIsolated yield.

With the established optimum reaction conditions, the substrate scope and generality of the present MCR was explored by using a wide variety of aromatic/hetero aromatic aldehydes (1a-x), thiosemicarbazide (2) and 3-(2-bromoacetyl)-2H-chromen-2-one (3) (Table 3). The parent benzaldehyde (1a) reacts with thiosemicarbazide (2), 3-(2-bromoacetyl)-2Hchromen-2-one (3) to form the corresponding product (4a) in 98% isolated yield. Benzaldehyde bearing electron-releasing groups (4-OMe (1b), 4-OH (1c), 3-OH (1d), 2-OH (1e) and 3-Oph (1f) groups) at different positions on the ring reacted efficiently with thiosemicarbazide (2) and 3-(2-bromoacetyl)-2H-chromen-2-one(3) to give the desired products (4b, 4c, 4d, 4e and 4f) in excellent isolated yields in the range of 94 to 98%. To our delight, the structure of 4b was confirmed by Xray crystallography (Fig. 1). Benzaldehyde with electronaccepting groups (4-NO₂ (1g) and 4-CN (1h)) present at different positions on the ring showed good reactivity with thiosemicarbazide (2) and 3-(2-bromoacetyl)-2H-chromen-2one(3) to afford the products 4g and 4h in good isolated yields 96 and 94%, respectively. Furthermore, the di substituted benzaldehydes (3-Cl-4-OH (1i), 3-Br-4-OH (1j), 4-OH-3-OMe (1k), 2-OH-5-OMe (1l), 2-OH-3-OMe (1m), 2,4-diOMe (1n) 2,5diOMe(1o), 3-OEt-2-OH(1p), 3-OEt-4-OH (1q), 3,5-di bromo (1r) and 2,6-di chloro (1s)) were also well-tolerated, providing the desired products 4i-4s in good isolated yields that ranged from 90 to 96%. Further, cinnamaldehyde (1t) underwent the reaction to give the corresponding product 4t in 96% isolated yield. 2-napthaldehyde (1u) afforded the corresponding product (4u) in 95% isolated yield. Interestingly, substituted hetero-aromatic aldehydes like 4-methylthiazole-5carboxaldehyde (1v), 2-aminonicotinaldehyde (1w) and 2chloro-8-methylquinoline-3-carbaldehyde (1x) reacted well with thiosemicarbazide (2), 3-(2-bromoacetyl)-2H-chromen-2one(3) to afford the desired products, 4v, 4w and 4x in good isolated yields, 95, 93 and 92%, respectively.

Table 3. Synthesis of HTC derivatives of aldehydes/ketones(4a-4ak) using various aldehydes/ketones, thiosemicarbazideand 3-(2-bromoacetyl)-2H-chromen-2-one.^[a]



aReagents and conditions: Aldehydes/ketones (1) (10.0 mmol), thiosemicarbazide (2) (10.0 mmol), 3-(2-bromoacetyl)-2H-chromen-2-one (3) (10.0 mmol), MMT K10 clay (12.5 wt-%) in water at RT.

Inspired by the above results, the scope of the present MCR strategy was extended to a variety of aromatic ketones (Table 3). To check the feasibility, a model reaction was conducted by employing acetophenone (1y), thiosemicarbazide (2) and 3-(2-bromoacetyl)-2H-chromen-2-one (3) under the optimized reaction conditions for 30 min at RT. It was found that the yield of the desired product, 4y was 97 %. Acetophenone with electron-donating groups (4-Me (1z), 4-OMe (1aa), 3-OMe (1ab), 4-OH (1ac) and 3-OH (1ad)) at different positions on the ring showed good reactivity towards this type of transformation to produce the corresponding products (4z-4ad) in good to excellent isolated yields that ranged from 94 to 96%. Acetophenone bearing electron-withdrawing groups (4-Br (1ae), 4-F (1af) and 4-NO₂ (1ag)) at *para* position on the aromatic ring were also converted into the corresponding products (4ae-4ag) in good

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isolated yields. Benzophenone (1ah) also undergoes the reaction to obtain the corresponding product 4ah in 94% isolated yield. Further, 1-acetylnapthalene (1ai) and 2-acetylnapthalene (1aj) reacted well with thiosemicarbazide (2) and 3-(2-bromoacetyl)-2Hchromen-2-one (3) to afford the corresponding products, 4ai and 4aj in good isolated yields of 90% and 93%. Notably, the heterocyclic compound 3-acetylcoumarin (1ak) also reacted well under the optimized reaction conditions to give the desired product (4ak) in good isolated yields. From this study, it was concluded that the developed method was suitable for a wide variety of aldehydes/ketones (mono substituted (both electron-deficient and electron-rich). di substituted and hetero aromatic aldehydes/ketones) under the established reaction conditions.

Single Crystal XRD Analysis

Golden yellow single crystals of (E)-3-(2-(2-(4methoxybenzylidene)hydrazinyl)thiazol-4-yl)-2H-chromen-2-one (**4b**) were grown in a mixture of methanol and DMSO (a few drops) by slow evaporation method. Molecular structure of **4b** was determined by X-ray crystallography (Fig. 1). From this study, it was identified that the two independent molecules (molecule A and B) were oriented in the same way with a monoclinic P2₁/c space



Figure 1. Molecular structures of (*E*)-3-(2-(2-(4-methoxybenzylidene) hydrazinyl)thiazol-4-yl)-2H-chromen-2-one (4b) (50% probability).

Mechanism

A plausible mechanism for the formation of HTCs (4) in the presence of MMT K10 clay is depicted in Scheme 2. The two NH₂ groups of thiosemicarbazide (2) react with the K10 clay activated carbonyl group of both aldehyde/ketone (1) and 3-(2-bromoacetyl)-2H-chromen-2-one (3) in water to obtain diimine (I). Subsequently, clay promoted internal S_N2 displacement of bromide ion of diimine (I) to form dihydro HTCs (II) followed by a proton shift to obtain HTCs (4).



 Scheme 2. A plausible mechanism for the formation of HTCs (4) catalyzed by View Article Online

 MMT K10 clay in water.
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Reusability of the catalyst

The reusability of MMT K10 clay catalyst was investigated in the reaction of 4-methoxy benzaldehyde (1b) (10.0 mmol), thiosemicarbazide (2) (10.0 mmol) and 3-(2-bromoacetyl)-2Hchromen-2-one (3) (10.0 mmol) under the optimized reaction conditions. After completion of the reaction, 10 mL of ethyl acetate was added to the reaction mixture and the spent catalyst was separated by filtration under vacuum. The recovered catalyst was washed with ethyl acetate (2.0 mL) and then 1.0 M HCl (5.0 mL) after each use. Finally, the recovered catalyst was dried under vacuum. To check the catalytic activity, the recovered catalyst was reused for 7 times under the optimized reaction conditions. The study revealed that the obtained yields of the product, 4b were 98, 98, 98, 98, 97, 97 and 97% for first, second, third, fourth, fifth, sixth and seventh cycles, respectively (Fig. 2). It is worthy to mention that the catalytic efficiency of the recovered catalyst is almost same as compared with the fresh catalyst.



Figure 2. Efficiency of MMT K10 clay catalyst.

Scalability of the method

The scalability of the process was then examined by the reaction of 1b, 2 and 3 in the presence of MMT K10 clay (12.5 wt%) in H_2O at RT in different gram scale reactions, 2.5, 5.0, 7.5 and 10 grams. The yields of product 4b were obtained as 98%, 97%, 96% and 96%. Hence, it could be concluded that the developed procedure is efficient, practical and greener alternative for the gram-scale production of HTCs (4).

Photophysical Properties

Based on recent report on structurally similar systems, it is assumed that the synthesized HTCs of aromatic aldehydes/ketones exhibit an intra molecular charge transfer (ICT) transitions due to their donor-acceptor (D-A) type structure.^{12a} The ICT transitions are highly sensitive to solvent polarity; hence the solvatochromic studies were conducted

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on 4b. The solvatochromic effect was studied by recording the absorption and emission spectra of 4b in different solvents like toluene, chloroform (non-polar solvents), ethyl acetate (EtOAc), acetonitrile, DMSO (polar aprotic solvents) and MeOH (polar protic solvent) at the concentration of 1.0 x10⁻⁵M (Fig. 3). A 10 nm red shift was found in absorption and 121 nm red shift was observed in emission bands of the luminophore, 4b with increasing the polarity of solvents from toluene to CH₃OH. Hence, the study revealed that the emission of 4b was much influenced by the polarity of solvent (Fig. 3). Interestingly, longer shifts towards to longer wavelength (bathochromic shift) from non-polar solvents, toluene (479 nm) and CHCl₃ (511 nm) to polar aprotic & polar protic solvents, EtOAc (532 nm), ACN (570 nm), DMSO (600 nm) and MeOH (596 nm) were noticed in the emission spectrum of 4b. Further, Stokes shift of 4b was also increased from non-polar to polar solvents, toluene ($\Delta v = 8535 \text{ cm}^{-1}$) < CHCl₃ ($\Delta v = 10016 \text{ cm}^{-1}$) < EtOAc ($\Delta v = 10877$ cm^{-1}) > ACN ($\Delta v = 12042 cm^{-1}$) < DMSO ($\Delta v = 12152 cm^{-1}$) < MeOH $(\Delta v = 12461 \text{ cm}^{-1})$. This might be attributed to the occurrence of ICT transitions in 4b and the effect solvent polarity. Hence, 4b is a D-A type structure.¹² Further, the Lippert-Mataga plot of Stokes shifts (Δv) versus solvent polarity function (Δf) was examined for 4b which showed good linear correlation with the solvent polarity (Table 4 & Fig. 4).



Figure 3. Normalized absorption (solid lines) and emission spectra (dotted lines) of **4b** in different solvents at 1.0 x10⁻⁵M.

Table 4. Lippert-Mataga Plot data for 4b.

Solvent $\lambda_{abs}(nm)$		$\lambda_{em}(nm)$	Δf	Δν (cm ⁻¹)
				$(\Delta v = v_{abs} - v_{em})$
PhMe	340	479	0.01	8535
CHCl ₃	338	511	0.15	10016
EA	337	532	0.18	10877
ACN	338	570	0.31	12042
DMSO	347	600	0.27	12152
MeOH	342	596	0.31	12461



Figure 4. The relationship between Stokes shifts (Δv) and solvent polarity function (Δf) for the compound **4b** in different solvents.

The photophysical properties of a series of D-A type HTCs of aromatic aldehydes/ketones (4) were recorded in chloroform at the concentration of 1.0 x10⁻⁵M (Fig. 5). The measured absorption and emission maxima positions, molar extinction coefficients (ε), Stoke shifts and optical band gaps (E_g^{opt}) are presented in Table 5. The study disclosed that the electron releasing groups (OMe, -OH, -OPh, di-OMe, -OMe-OH, -OEt-OH, 3-Cl-4-OH etc.) at different positions on the aromatic ring of aldehydes/ketones of HTC moiety have shown unfordable influence on the absorption and emission properties of the studied HTC luminophores (4). The electron donating groups at para and meta positions (4-OMe (1b), 4-OH(1c), 3-OH(1d), 3-OPh(1f)) on the aromatic ring of aldehydes were bathochromically shifted with large Stokes shift as compared with electron donating hydroxyl group at ortho position (2-OH, (1e)). Further, the di substituted benzaldehydes, 3-Cl-4-OH (1i), 2,4diOMe (1n), 2,5-diOMe (1o), 4-OH-3-OMe and 4-OH-3-OEt (1q), were red shifted with large Stokes shift as compared with 2-OH-5-OMe (11) and 2-OH-3-OEt (1p) benzaldehydes. Cinnamaldehyde (1t) was red shifted with large Stokes shift than the benzaldehyde (1a) and naphthaldehyde (1u). It was also noticed that the acetophenone (1y) was red shifted with large Stokes shift than the 2-acetylnapthalene (1aj). p-Hydroxyacetophenone (1ac) was bathochromically shifted with large Stokes shift as compared with p-Me (1z), p-OMe (1aa) and m-OH (1ad) acetophenones. Further, the study revealed that the HTCs of ketones were brightly fluorescent as compared with HTCs of aldehydes. To our delight, the examined HTCs of aromatic aldehydes and ketones (4) exhibited bright blue, violet and yellowish green emission with large Stokes shift from the corresponding absorption maxima (Fig. 5 and Table 5). Hence, the synthesized HTCs (4) may have potential applications in various fields like biomedical research and organic electronics.

Further, the quantum yield of HTC compounds (4) were determined by using quinine sulphate as a standard reference compound ($\phi_F = 0.545$ in 1.0N H₂SO₄). The obtained results are summarized in Table 5. From this study, it was noticed that the quantum yields of HTCs (4) were ranged from 1.90 to 24.17 % in chloroform.

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Figure 5. a) Photographs of HTCs of aromatic aldehydes in CHCl₃under the UV light at 365 nm; b) Normalized absorption (solid lines) and emission spectra (dotted lines) of HTCs of aromatic aldehydes in CHCl₃ (1.0×10^{-5} M); c) Photographs of HTCs of aromatic ketones in CHCl₃ under the UV light at 365 nm; d) Normalized absorption (solid lines) and emission spectra (dotted lines) of HTCs of aromatic ketones in CHCl₃ (1.0×10^{-5} M).

Electrochemical properties

The electrochemical properties of HTCs were determined by cyclic voltammetry using 0.5mM chloroform solution of HTCs along with 0.1 M tetrabutyl ammonium hexaflourophosphate as a supporting electrolyte. Platinum disk, platinum wire and Ag/Ag⁺ (satd. KCl) were used as working electrode, counter electrode and reference electrode, respectively. All the CV scans were recorded in the potential range –0.2 to 1.6 V vs Ag/AgCl (satd. KCl) readings were

taken at a scan rate of 100 mV/s. Some of the representative cyclic voltammograms (CVs) of HTC compounds (4) are showed in orige as Other CVs of HTCs (4) are shown in Supplementary information (Fig. S4). Most of the cyclic voltammograms of HTCs (4) were in quasi reversible nature (Fig. 6 & Fig. S4). The HOMO energy levels were calculated from the onset of oxidation potential and the LUMO energy levels were calculated from the HOMO energy levels and the optical band gap (Egopt) (UV-Vis absorption). The obtained data is presented in Table 5. The study revealed that the HOMO and LUMO energy levels of HTCs that ranged from -5.65 eV to -5.22 eV and -2.67 eV to -2.17 eV, respectively. To our delight, most of the HOMO and LUMO levels of the studied HTC compounds were comparable with the reported hole transport materials (HTMs) like N,N'-di-(naphthalen-1-yl)-N,N'-diphenylbenzidine (NPB) (HOMO/LUMO -5.5/-2.4 eV),^{13b} N, N-di(naphthaien-1-yl)-N,N,10-triphenyl-10Hspiro(acridine-9,9'-fluorene)-2,7-diamine (STNPB) (HOMO/LUMO eV),13c -5.35/-2.45 4,4,4"-tris[(2,3,4,5tetraphenyl)phenyl]phenylamine (TTPPPA) (HOMO/LUMO -5.46/-2.36 eV),^{13d} N,N'-bis-(1-naphthyl)-N,N'-diphenyl benzidine (α -NPD)(HOMO/LUMO -5.43/-2.33 eV),^{13e} 4,4'-[bis-((4-di-nhexylamino)benzylideneamino)]stilbene (DHABS) (HOMO/LUMO -5.57/-2.73 eV)^{13f} and 2-[1{4-(N-phenylnaphthalen-1-amino)phenyl-3,4-,5,6-tetraphenylbenzene-2-yl]-5-(N-phenyl naphthalen-2-amino) pyridine (2-PNAP-TB) (HOMO/LUMO -5.25/-2.16 eV). Hence, the HTC compounds are capable to act as hole transporting materials.¹³ Further, most of the HTC compounds were equipped with low-lying HOMO energy levels than the threshold for air oxidation (approximately -5.2 eV)¹⁴ leading to a good stability under ambient conditions. From this study, it is concluded that the electrochemical behaviour of HTCs are significantly influenced by the electron donating groups present at different positions on the aromatic ring of aldehydes/ketones.





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Figure 6. a) Representative cyclic voltammograms of HTCs of aromatic aldehydes (4a-4d) in CHCl₃; b) Representative cyclic voltammograms of HTCs of aromatic ketones (4y, 4z, 4aa & 4ac) in CHCl₃ (0.1 M Bu_4NPF_6 in CHCl₃) at a scan rate of 100 mV/s.

 Table 5. Photophysical and electrochemical data of HTCs of various aromatic aldehydes/ketones (4).

Compd	λ _{max} (nm)ª	λ _{edge} (nm)	λ _{emis} (nm) ^b	ε (L m ⁻¹ cm ⁻¹) ^c	Stokes Shift (cm ⁻¹) ^d	ф _{ет} е (%)	Eg ^{opt} (eV) ^f	E ^{ox} (onset)	Е _{номо} (eV) ^g	E _{LUMO} (eV) ^t
4a	342	416	439	30000	6460	17.98	2.98	0.95	-5.37	-2.39
4b	338	419	511	26000	10016	11.37	2.96	1.10	-5.52	-2.56
4c	349	408	479	32000	7776	17.02	3.04	1.15	-5.57	-2.53
4d	346	411	476	28000	7893	17.33	3.02	1.03	-5.45	-2.43
4e	347	402	437	24000	5935	8.02	3.08	0.93	-5.35	-2.27
4f	347	417	476	22000	7893	9.57	2.97	1.14	-5.56	-2.59
4k	339	385	491	20000	9131	1.90	3.22	0.97	-5.39	-2.17
41	355	412	435	24000	5180	2.06	3.01	1.13	-5.55	-2.54
4n	353	413	474	26000	7231	7.37	3.00	0.89	-5.31	-2.31
40	359	417	497	30000	7734	8.25	2.97	1.05	-5.47	-2.50
4р	344	391	409	20000	4619	6.36	3.17	0.92	-5.34	-2.17
4q	351	408	474	35000	7392	8.03	3.04	0.80	-5.22	-2.18
4t	358	422	505	53000	8130	2.74	2.94	0.96	-5.38	-2.44
4u	344	408	431	30000	5867	6.08	3.04	0.91	-5.33	-2.29
4y	336	415	506	34000	9999	21.36	2.99	0.92	-5.34	-2.35
4z	347	416	475	20000	7765	24.17	2.98	1.23	-5.65	-2.67
4aa	357	412	510	43000	8403	11.49	3.01	0.94	-5.36	-2.35
4ab	346	421	474	20000	7804	7.00	2.94	0.91	-5.33	-2.39
4ac	337	419	507	13000	9949	12.56	2.96	1.14	-5.56	-2.60
4ad	336	419	492	13000	9436	10.76	2.96	1.09	-5.51	-2.55
4aj	350	419	472	36000	7384	3.94	2.96	0.97	-5.39	-2.43

[a] Absorption maxima measured in CHCl₃ at 1.0 x10⁻⁵M. [b] Emission maximum in CHCl₃ at 1.0 x10⁻⁵M. [c] Molar extinction coefficient at 1.0 x10⁻⁵M. [d] Stokes shift $\Delta v = v_{abs}-v_{emis}$. [e] Quantum yield with standard reference to quinine sulphate ($\Phi_{em} = 0.545$ in 1 N H₂SO₄). [f] $E_g^{opt} = 1240/\lambda_{edge}$. [g] $E_{HOMO} = -[E_{ox} (onset) - E_{FOC} + 4.8]$ ($E_{FOC} = 0.38$ eV (FOC/FOC⁺ vs. Ag/AgCl)). [h] $E_{LUMO} = E_{HOMO} + E_g^{opt}$.

Experimental

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General procedure for the synthesis of hydrazinyl thiazolyl coumarins (HTCs) (4):

round-bottomed flask (25 mL) was Α charged with aldehydes/ketones (1) (10.0 mmol), thiosemicarbazide (2) (10.0 mmol), 3-(2-bromoacetyl)-2H-chromen-2-one (3) (10.0 mmol), MMT K10 clay (12.5 wt.-%) and H₂O (10.0 mL). The reaction mixture of was stirred at room temperature for 20-40 min. After completion of the reaction as indicated by TLC, 5.0 mL of ethyl acetate was added to the reaction mass and the catalyst was recovered by filtration followed by washing with ethyl acetate (2.0 mL) and 1.0 M HCl (5.0 mL) under vacuum. The organic layer was separated, dried over anhydrous Na₂SO₄ and concentrated under reduced pressure to afford the pure product (4). The structures of the synthesized compounds were confirmed by ¹H NMR, HRMS and mass spectral analysis and the structure of 4b was confirmed by X-ray crystallography.

General procedure for gram scale (10 g scale) synthesis of (*E*)-3-(2-(2-(4-methoxybenzylidene)hydrazinyl)thiazol-4-yl)-2H-chromen-2one (4b): A mixture of 4-methoxybenzaldehyde (1b) (0.0735 moles), thiosemicarbazide (2) (0.0735) and 3-(2-bromoacetyl)-2H-chromen-2-one (3) (0.0735 moles) in H₂O (40 mL) was stirred in the presence of MMT K10 clay (12.5 wt.-%) at RT for 20–40 min. After completion of the reaction as indicated by TLC, 30 mL of ethyl acetate was added to the reaction mass and the catalyst was recovered by filtration followed by washing with ethyl acetate (10.0 mL) and 1.0 M HCl (30 mL) under vacuum. The organic layer was separated, dried over anhydrous Na₂SO₄ and concentrated under reduced pressure to afford the pure product (4b).

Conclusions

A practical green MCR strategy has been demonstrated for the synthesis of a series of fluorescent HTCs of aromatic aldehydes/ketones (4) in good to excellent isolated yields (90-98%) by a 3-component reaction of readily available aromatic aldehydes/ketones (1) thiosemicarbazide (2) 3-(2-bromoacetyl)-2Hchromen-2-one (3) catalyzed by MMT K10 clay in water at RT for 20-40 min. Construction of C-N, C=N and C-S bonds in a single step operation, simple workup procedure, high product yields in short reaction times with no need of further purification and scaled up to a gram level are the notable features of the present MCR. Besides, the developed MCR provides a convenient greener access to HTCs as it reduces the steps and waste generation and employs an environmentally benign, inexpensive, readily available and reusable MMT K10 clay catalyst in water. Hence, the established MCR procedure is sustainable and greener alternative to the existing procedures for the synthesis of wide range of HTCs. Photo physical properties of the synthesized D-A type HTCs aldehydes/ketones were also examined. Solvent polarity had more impact on the emission maxima of 4b. Most of the HTC compounds exhibited bright fluorescence in chloroform with emission maxima ranging from 409 to 511 nm. The title compounds with electron donating groups at para/meta positions (p-OMe, p-OH, m-OH, m-OPh) on the aromatic ring of aldehydes/ketones were bathochromically shifted with large Stokes shifts. Further, the HOMO and LUMO energy

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levels of HTC compounds are well matched with the HOMO and LUMO levels of the reported hole transporting materials. Therefore, these compounds can be used as hole transporting materials. Because of these attractive features, HTC compounds might have wide variety of applications in organic electronics. Deeper studies into the fluorescence properties and further application of the synthesized fluorophores (4) are underway in our laboratory.

Conflicts of interest

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There are no conflicts to declare.

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Synthesis, Photophysical and Electrochemical Properties of Donor-Acceptor Type Hydrazinyl Thiazolyl Coumarins

G. Kumar, G. Trivikram Reddy, B. Ramakrishna, Y.V. Divyasri, L. Subramanyam Sarma and N. C. Gangi Reddy*

A practical green MCR strategy has been developed for the synthesis of D-A type hydrazinyl thiazolyl coumarins catalyzed by an environmentally compatible MMT K10 clay in water at RT.

