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Synthesis and photophysical properties of novel chloroquinoline based chalcone derivatives containing 1,2,3-triazole moiety

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ABSTRACT

A series of novel chloroquinoline based chalcones containing 1,2,3-triazole moiety were synthesized. All new compounds were characterized by ^1H NMR, ^{13}C NMR, mass spectra and single crystal X-ray diffraction study. The absorbance, fluorescence spectra and quantum yield of all compounds were investigated in methanol. Photophysical properties of 1-(1-(7-chloroquinolin-4-yl)-5-methyl-1H-1,2,3-triazol-4-yl)-3-(3,4,5-trimethoxyphenyl)prop-2-en-1-one (3a) were investigated in detail. The effect of various solvents over emission spectra of 3a was studied using Kamlet–Taft and Catalan polarity scales. The quantum yield of 3a in various solvents was also recorded. The ground state and excited state dipole moments of compound 3a were determined using solvatochromic methods. The ground state dipole moment was estimated to be 1.081 D, while excited state dipole moment was found in the range of 11.969–3.801 D. Thermal stability of compound 3a and its precursor was also investigated using thermogravimetric analysis.

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1. Introduction

Development of new fluorescent molecules has attracted much attention during the past few years due to their increasing applications in wide range of electronic and optoelectronic devices related to telecommunications, optical computing, optical storage and optical information processing [1]. Chalcones constitute an important class of naturally occurring flavonoids exhibiting a wide spectrum of biological activities [2,3]. Chalcone derivatives are also important due to their photophysical properties and optical applications such as second harmonic generation materials in non-linear optics [4], photorefractive polymers [5], holographic recording materials [6], fluorescent probes for sensing of metal ions [7] and microenvironment in micelles [8]. Photophysical and spectroscopic properties of chalcones can be readily modified by the introduction of conjugation. 1,2,3-triazoles are privileged structures and have found applications as fluorescent brighteners [9], dyes [10], corrosion-retarding agents [11] and fluorescent metal ion sensors [12]. Triazole derivatives have also been studied for their optical brightening properties [13,14]. Substituted quinoline derivatives have rigid structure, wide energy gaps, high fluorescent quantum yield and are widely used as fluorescence materials and sensors for metal ions and biological molecules [15]. The fluorescent characteristics of a molecule mainly depend on the

molecular structure, such as conjugate system, coplanarity and rigidity. Thus there is a considerable interest to increase the conjugation in molecules in order to acquire favorable physical properties required for specific applications [16].

Hence, our approach was to design newly conjugated derivatives with fluorescent properties that can be used as fluorescent material with diverse applications. There is no report on the photophysical properties of triazole, chalcone and quinoline heterocyclic conjugates. Introduction of 1,2,3-triazole unit and quinoline moiety into the chalcone structure can significantly improve the photophysical properties of chalcones by increasing overall conjugation. Thus, in present work we report the synthesis and photophysical properties of a novel series of fluorescent chalcones derivatives containing 1,2,3-triazole and chloroquinoline moieties. Further solvatochromism [17], dipole moment [18] and thermal characteristics were also studied.

2. Experimental

All chemicals were purchased from Spectrochem India and were used as received. Precoated aluminum plates (Silica gel 60F₂₅₄) from Merck were used to monitor reaction progress. IR (KBr) spectra were recorded on a PerkinElmer FTIR spectrophotometer and the values are expressed as ν_{max} cm^{-1} . The NMR (^1H and ^{13}C) spectra were recorded on Jeol JNM ECX-400P at 400 MHz and 100 MHz, respectively. The chemical shift values are

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recorded on δ scale and the coupling constants (J) are in Hertz. The mass spectra were recorded on an Agilent 6520-QTOF LCMS having ESI source in positive mode. X-ray intensity data was collected on an Oxford Diffraction Xcalibur CCD diffractometer with graphite monochromatic Mo K α radiation ($\lambda=0.71073$ Å) at temperature 298 K. Crystallographic data (excluding structure factors) for the structure have been deposited with the Cambridge Crystallographic Data Center with CCDC no. 1013869. These data can be obtained free of charge from the CCDC via www.ccdc.cam.ac.uk/data_request/cif. Ultraviolet–visible (UV–vis) absorption spectra were recorded on an Analytikjena specord 250 spectrophotometer. The fluorescence spectra were measured on a Cary Eclipse Fluorescence spectrophotometer. The quantum yield (ϕ) was measured by comparing the integrated photoluminescence intensities and the absorbance values with the reference fluorophore quinine sulfate (QS) according to Eq. (1), wherein ϕ is the quantum yield, I is the measured integrated emission intensity, η is the refractive index, and A is the optical density. The subscript R refers to the reference fluorophore of known quantum yield

$$\phi = \phi_R \frac{I_{AR}\eta^2}{I_{RA}\eta_R^2} \quad (1)$$

For all measurements, excitation wavelength was employed at 365 nm with slit width of 5 nm. The statistical calculations and linear fit were performed in Origin 7.0 program.

2.1. Procedure for synthesis of 4-azido-7-chloroquinoline (1)

A mixture of 4,7-dichloroquinoline (1.0 mmol), sodium azide (1.1 mmol) and PEG-400 (5 mL) was stirred at 60 °C for 1 h. The reaction was monitored by TLC (ethyl acetate–petroleum ether (40:60, v/v) as eluent). After completion of reaction as indicated by TLC, reaction mixture was allowed to cool to room temperature and water (20 mL) was added to reaction mixture. The precipitate formed was collected by filtration at a pump, and washed with water to afford crude product. The resulting product residue was crystallized from ethanol to yield the pure product 1 as colorless solid in 93% yield, m.pt 115–117 °C [19].

2.2. Procedure for the synthesis of 1-(1-(7-chloroquinolin-4-yl)-5-methyl-1H-1,2,3-triazol-4-yl)ethanone (2)

A mixture of 4-azido-7-chloroquinoline 1 (1.0 mmol) and acetylacetone (1.1 mmol) was placed in a 50 mL round-bottomed flask containing task specific basic ionic liquid [bmim]OH (10.0 mmol). The mixture was stirred at 80 °C for 15 min. After completion of the reaction as monitored by TLC using ethyl acetate:petroleum ether (70:30, v/v) as eluent, the reaction mixture was allowed to cool to room temperature and was quenched with water (10 mL). The precipitate formed was collected by filtration at a pump, washed with water and dried. The crude product was crystallized from ethanol to yield the pure 1-(1-(7-chloroquinolin-4-yl)-5-methyl-1H-1,2,3-triazol-4-yl)ethanone (2) as colorless solid in 92% yield.

Colorless solid; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 8.83 (d, 1H, $J=4.9$, ArH), 8.09 (d, 1H, $J=2.4$, ArH), 8.01 (d, 1H, $J=9.3$, ArH), 7.49 (m, 1H, ArH), 7.13 (d, 1H, $J=4.9$, ArH), 2.62 (s, 3H, COCH_3), 2.40 (s, 3H, CH_3); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) 190.26, 150.9, 149.1, 146.8, 141.20, 136.9, 131.45, 127.9, 123.8, 121.40, 119.9, 108.7, 27.56, 9.69; IR (KBr) ν_{max} cm^{-1} : 3021, 1656, 1612, 1560, 1435; MS (ESI) m/z calcd. for $\text{C}_{14}\text{H}_{11}\text{ClN}_4\text{O}$: 286.0621 found: 287.1201 ($\text{M}^+ + 1$).

2.3. General procedure for synthesis of triazolyl chalcones (3a–3o)

A mixture of the substituted aromatic aldehyde (1.0 mmol) and 1-(1-(7-chloroquinolin-4-yl)-5-methyl-1H-1,2,3-triazol-4-yl)

ethanone (2) (1.0 mmol) dissolved in ethanol (10 mL) was added slowly to an aqueous solution of potassium hydroxide (1.2 mmol) in water (5 mL). The reaction mixture was stirred at 0 °C firstly for 10 min, and then at room temperature for 3–4 h. The progress of reaction was monitored by TLC using ethyl acetate–petroleum ether (60:40, v/v) as eluent. After completion of reaction as indicated by TLC, the reaction mixture was filtrated and the solid so obtained was washed with cold water. The crude product obtained was crystallized from ethanol to yield pure derivatives 3a–3o in good yield.

2.4. Spectral data for triazolyl chalcones 3a–3o

2.4.1. 1-(1-(7-chloroquinolin-4-yl)-5-methyl-1H-1,2,3-triazol-4-yl)-3-(3,4,5-trimethoxyphenyl)prop-2-en-1-one (3a)

Pale yellow solid; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 9.14 (d, 1H, $J=4.4$ Hz, ArH), 8.28 (d, 1H, $J=2.2$ Hz, ArH), 8.00 (d, 1H, $J=16.12$ Hz, $\text{CH}_a=\text{CH}$), 7.89 (d, 1H, $J=16.12$ Hz, $\text{CH}=\text{CH}_b$), 7.58–7.56 (m, 1H, ArH), 7.43 (d, 1H, $J=4.4$ Hz, ArH), 7.35 (d, 1H, $J=8.8$ Hz, ArH), 6.95–6.94 (m, 2H, ArH), 3.95 (s, 3H, OCH_3), 3.93 (s, 3H, OCH_3), 3.90 (s, 3H, OCH_3), 2.54 (s, 3H, CH_3); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ : 183.84, 153.48, 151.31, 150.10, 144.60, 140.65, 140.15, 139.56, 138.26, 137.34, 131.08, 130.20, 129.88, 129.08, 123.75, 122.16, 121.76, 118.86, 106.01, 60.06, 56.28, 9.90; IR (KBr, cm^{-1}): $\nu_{\text{max}}=2926, 1665, 1605, 1578, 1502, 1416$; MS (ESI) m/z calcd. for $\text{C}_{24}\text{H}_{21}\text{ClN}_4\text{O}_4$: 464.1251 found: 465.1568 ($\text{M}^+ + 1$).

2.4.2. 1-(1-(7-chloroquinolin-4-yl)-5-methyl-1H-1,2,3-triazol-4-yl)-3-(4-methoxyphenyl)prop-2-en-1-one (3b)

Colorless solid; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 9.12 (d, 1H, $J=4.4$ Hz, ArH), 8.27 (d, 1H, $J=1.48$ Hz, ArH), 7.99 (d, 1H, $J=16.12$ Hz, $\text{CH}_a=\text{CH}$), 7.93 (d, 1H, $J=16.12$ Hz, $\text{CH}=\text{CH}_b$), 7.69 (d, 2H, $J=8.8$ Hz, ArH), 7.55–7.58 (m, 1H, ArH), 7.43 (d, 1H, $J=4.4$ Hz, ArH), 7.34 (d, 1H, $J=8.8$ Hz, ArH), 6.94 (d, 1H, $J=8.8$ Hz, ArH), 3.85 (s, 3H, OCH_3), 2.53 (s, 3H, CH_3); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ : 183.93, 161.89, 151.35, 149.97, 144.23, 144.00, 139.83, 139.58, 137.26, 130.76, 129.88, 129.07, 127.50, 123.82, 122.26, 120.29, 118.79, 114.42, 55.14, 9.96; IR (KBr, cm^{-1}): $\nu_{\text{max}}=2927, 1661, 1590, 1511, 1423$; MS (ESI) m/z calcd. for $\text{C}_{22}\text{H}_{17}\text{ClN}_4\text{O}_2$: 404.1040 found: 405.1091 ($\text{M}^+ + 1$).

2.4.3. 1-(1-(7-chloroquinolin-4-yl)-5-methyl-1H-1,2,3-triazol-4-yl)-3-(4-(trifluoromethyl)phenyl)prop-2-en-1-one (3c)

Colorless solid; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 9.13 (d, 1H, $J=5.12$ Hz, ArH), 8.27 (d, 1H, $J=2.2$ Hz, ArH), 8.16 (d, 1H, $J=16.12$ Hz, $\text{CH}_a=\text{CH}$), 7.94 (d, 1H, $J=16.12$ Hz, $\text{CH}=\text{CH}_b$), 7.82 (d, 2H, $J=8.08$ Hz, ArH), 7.67 (d, 1H, $J=8.08$ Hz, ArH), 7.55–7.58 (m, 1H, ArH), 7.43 (d, 1H, $J=4.4$ Hz, ArH), 7.32 (d, 1H, $J=8.8$ Hz, ArH), 2.54 (s, 3H, CH_3); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ : 183.62, 151.36, 150.03, 143.68, 142.20, 140.38, 139.32, 138.05, 137.27, 131.84, 129.92, 129.17, 128.83, 125.89, 125.85, 124.79, 123.66, 122.12, 118.76, 9.96; IR (KBr, cm^{-1}): $\nu_{\text{max}}=2926, 1669, 1609, 1431, 1309$; MS (ESI) m/z calcd. for $\text{C}_{22}\text{H}_{14}\text{ClF}_3\text{N}_4\text{O}$: 442.0808 found: 443.1201 ($\text{M}^+ + 1$).

2.4.4. 4-(3-(1-(7-chloroquinolin-4-yl)-5-methyl-1H-1,2,3-triazol-4-yl)-3-oxoprop-1-enyl)benzotrile (3d)

Colorless solid; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 9.13 (d, 1H, $J=4.4$ Hz, ArH), 8.28 (d, 1H, $J=1.48$ Hz, ArH), 8.16 (d, 1H, $J=16.12$ Hz, $\text{CH}_a=\text{CH}$), 7.91 (d, 1H, $J=16.12$ Hz, $\text{CH}=\text{CH}_b$), 7.80 (d, 2H, $J=8.8$ Hz, ArH), 7.71 (d, 2H, $J=8.8$ Hz, ArH), 7.56–7.58 (m, 1H, ArH), 7.43 (d, 1H, $J=4.4$ Hz, ArH), 7.31 (d, 1H, $J=9.52$ Hz, ArH), 2.54 (s, 3H, CH_3); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ : 183.45, 151.38, 150.05, 143.67, 141.59, 140.53, 139.31, 139.02, 137.36, 132.69, 129.99, 129.21, 129.03, 125.71, 123.63, 122.12, 118.78, 113.65, 10.00; IR (KBr, cm^{-1}): $\nu_{\text{max}}=2925, 1667, 1611, 1560, 1429$; MS (ESI) m/z calcd. for $\text{C}_{22}\text{H}_{14}\text{ClN}_5\text{O}$: 399.0887 found: 400.1024 ($\text{M}^+ + 1$).

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