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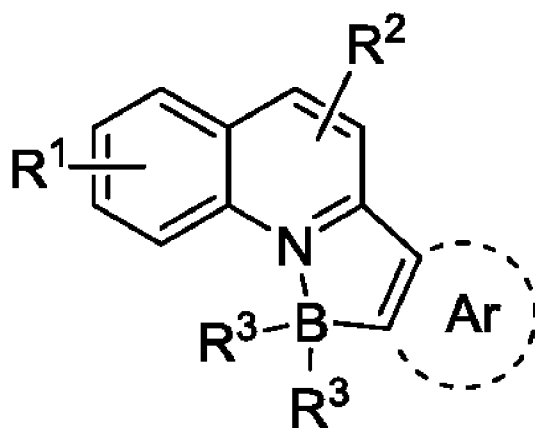
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(54) **Title:** N, C-CHELATE FOUR-COORDINATE ORGANOBORONS WITH FULL COLOUR TUNABILITY



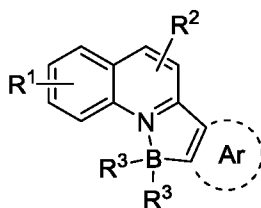
(I)

(57) **Abstract:** The present invention relates to novel full-color tunable light emitter based on N, C-chelate four-coordinate organoborons having excellent Quantum yield, stokes shift and solvate chromism of Formula (I).

N, C-CHELATE FOUR-COORDINATE ORGANOBORONS WITH FULL COLOUR TUNABILITY

FIELD OF THE INVENTION:

The present invention relates to novel full-color tunable light emitter based on N,C-chelate four-coordinate organoborons having excellent Quantum yield, Stokes shift and solvate chromism of Formula (I);



Formula (I)

BACKGROUND AND PRIOR ART:

Organic optoelectronic devices are becoming widely desirable due to various reasons such as the organic devices are cost effective, the inherent properties of the organic material such as flexibility, fluorescent properties, color tunability using functionalized molecules make them suitable for particular applications.

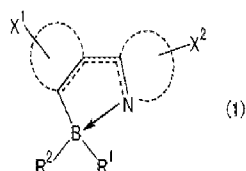
Designing of luminescent organic material plays a pivotal role in development of optoelectronic devices with improved energy consumption. Research is more focused on providing solid light emitters for their practical applications in optoelectronic devices, such as organic light-emitting diodes. The solid state fluorescent material known in the art are heavily relied on mere functionalization of existing fluorophores. However, considering the demand of solid light emitters in material science and biology, there is an urgent need for the identification of novel core structures, with full colour-tunability, capable of emitting light in the aggregation state.

Organoborons have attracted considerable attention in the scientific fraternity due to their unique electronic structure and interesting optical property derived from the intrinsic p_{II}-p* conjugation between the vacant p_x-orbital of the boron atom and the Π* orbital of the p-conjugated framework.

The most potential examples of fluorescent organoboron compounds are borondipyrromethene (BODIPY) dyes and its analogues which are only emissive in dilute solutions and their fluorescence is quenched severely in the aggregate state [L. Bonardi, H.

Kanaan, F. Camerel, P. Jolinat, P. Retailleau, R. Ziessel, *Adv. Funct. Mater.* 2008, 18, 401]. Hence, a more robust highly emissive solid organoborons are needed.

PCT application WO2011099331, discloses a novel boron-containing compound which is useful as a light-emitting material for organic EL elements or N-type semiconductors; a boron-containing polymer obtained using the compound; and a process for the preparation of the boron-containing compound, which enables low-cost production of the boron-containing compound and the boron-containing polymer. A light-emitting material which contains a boron-containing compound that has a boron atom and a double bond and that has a specific structure. A luminescent material comprising a boron-containing compound having a boron atom and a double bond, the boron-containing compound represented by the following formula (1);



Article titled “Aggregation-induced emission and efficient solid-state fluorescence from tetraphenylethene-based N,C-chelate four-coordinate organoborons” by Zujin Zhao et al. published in *Chemistry European Journal*, 2013, 19, 11512 – 11517 reports boron compounds containing the TPE moiety and N,C-chelate of formula 2 and to the synthesis thereof. Here quantum yield of chelate compounds are 0.40, 0.94 and 0.019.

Article titled “Synthesis of pyridine-borane complexes via electrophilic aromatic borylation” by Naoki Ishida et al. published in *Journal of Organic Chemistry*, 2010, 75, 8709–8712 reports synthesis of Pyridine-borane complexes from 2-arylpyridines through an electrophilic aromatic borylation reaction with BBR_3 .

Article titled “From blue to red: syntheses, structures, electronic and electroluminescent properties of tunable luminescent N,N chelate boron complexes” by Q.D. Liu *et al.* published in *Advances Functional Materials*, 2005, 15,1, pp 143–154 reports A comprehensive study of a series four-coordinate boron compounds with the general formula of $\text{BPh}_2(\text{N,N})$, where N,N are bidentate chelate ligands containing both neutral and negatively charged nitrogen donor atoms has been conducted. The structures of the boron complexes were examined via single-crystal X-ray diffraction.

Article titled “Four-coordinate organoboron compounds with a π -conjugated chelate ligand for optoelectronic applications” by Ying-Li Rao *et al.* published in *Inorganic*

Chemistry, 2011, 50 (24), pp 12263–12274 reports Four-coordinate organoboron compounds that possess a conjugated chelate ligand have found important applications in advanced materials including emitters and electron-transport materials for organic light-emitting diodes, photochromic materials, and sensing and imaging materials. The recent
5 advances in optoelectronic applications of four-coordinate organoboron compounds are presented in this article.

Article titled “Cooperative catalysis with metal and secondary amine: synthesis of 2-substituted quinolines via addition/cycloisomerization cascade” by Nitin T. Patil *et al.* published in *Journal of Organic Chemistry*, 2010, 75 (20), pp 6961–6964 reports a
10 cooperative catalytic system, consisting of CuI and pyrrolidine, has been developed for an efficient synthesis of 2-substituted quinolines. A combination of both the catalysts is necessary; the use of either catalyst alone does not give the product.

Article titled “Photochromic four-coordinate N,C-chelate boron compounds” by Ying-Li Rao *et al.* published in *Coordination Chemistry Reviews*, 2012, 256, 5–8, pp 759–770 reports
15 four-coordinate organoboron compounds with a N,C-chelate backbone have been found recently to display an unusual photoisomerization phenomenon with a distinct change of color.

Article titled “Enhancing the photochemical stability of N,C-chelate boron compounds: C–C bond formation versus C=C bond cis, trans-isomerization.” by Chul Baik
20 *et al.* published in *Journal of American Chemical Society*, 2009, 131, 14549–14559 reports N,C-Chelate boron compounds such as B(ppy)Mes₂ (ppy = 2-phenylpyridyl, Mes = mesityl) have been recently shown to undergo a facile and reversible C–C/C–B bond rearrangement upon irradiation with UV-light, quenching the emission of the sample and limiting their use in optoelectronic devices. It also disclosed Stoke’s shift.

Article titled “Steric and electronic influence on photochromic switching of N,C-chelate four-coordinate organoboron compounds” by Hazem Amarneet *et al.* published in *Chemistry - A European Journal*, 2010, 16(16):4750–61 reports a four-coordinate organoboron
25 compound B(ppy)Mes₂ (1, ppy=2-phenylpyridyl, Mes=mesityl) was previously found to undergo reversible photochromic switching through the formation/breaking of a C-C bond, accompanied by a dramatic color change from colorless to dark blue.
30

Article titled “N^N- and N^C chelate four-coordinate organoboron compounds: synthesis, properties and applications” by Jiasheng Lu published as thesis 2013 reports the synthesis of N^N- and N^C-chelate four coordinate organoboron compounds and the investigation of their photophysical and photochemical properties.

US Pat. Appl. No. 20120253044 discloses organoboron compounds are described that upon exposure to light, absorb light and isomerize and form a dark-colored isomer. The dark-colored isomer converts back to the colorless isomer upon removal of light, or exposure to oxygen or heat. Such compounds can be added into polymeric matrices such as films.

Inspired by the prior art reports, the present inventors felt a need to provide novel class of N, C-chelate four-coordinate organoborons with different emission colors. The present inventors further observed that with the appropriate choice of the substituents on boron or quinoline, full colortunability can be obtained which can span the whole visible region.

OBJECTIVE OF THE INVENTION:

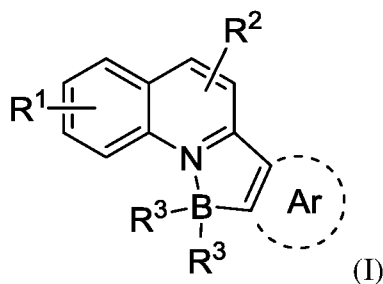
The main objective of the present invention is to provide novel class of N, C-chelate four-coordinate organoborons of Formula (I) with different emission colors useful in biology and in optoelectronic devices.

The another objective of the present invention is to achieve colour tunability both in solid and solution state through the substituent's on either quinolines or on boron centre of N, C-chelate four-coordinate organoborons of Formula (I).

Still another objective of the present invention is to provide molecular fluorophores based on N, C-Chelate four-coordinate organoborons which exhibit fluorescence with a large Stokes shift, range of quantum yield and exhibit solvatochromism.

SUMMARY OF THE INVENTION:

Accordingly, the present invention provides N,C-Chelate four-coordinate organoborons of Formula (I), wherein said organoborons exhibit tunable emission colours that cover the whole visible region, useful in bio imaging and in optoelectronic devices



wherein,

R^1 , R^2 and R^3 are selected independently from hydrogen, halogen, (un)substituted alkyl, (un)substituted aryl, (un)substituted heteroaryl, (un)substituted heterocyclic group; more particularly, R^1 , R^2 is H; R^3 is selected from methyl, ethyl, "Octyl, phenyl.

- 5 'ringAr' represent (un)substituted aryl, (un)substituted heteroaryl, (un)substituted heterocyclic group, more particularly, Ar is selected from benzothiophenyl, pyrenyl, phenanthrenyl, N,N-diphenyl aniline ($\text{Ph}_2\text{N}-\text{C}_6\text{H}_4$), Carbazole- C_6H_4 , dimethyl aniline ($\text{Me}_2\text{N}-\text{C}_6\text{H}_4$).

10 In an embodiment, the present invention provides N, C-Chelate four-coordinate organoborons of Formula (I) that exhibit color tunability both in solid and solution state that can span the entire region of visible spectrum.

In another embodiment, the present invention provides novel full-color tunable light emitter based on N,C-chelate four-coordinate organoborons having excellent Quantum yield, stokes shift and solvatochromism of Formula (I).

15 In still another embodiment, the present invention provides a process for synthesis of N, C-Chelate four-coordinate organoborons of Formula (I) comprising the steps of:

- a) reacting 2-amino benzaldehyde with suitable alkyne in presence of Au(I) as catalyst and an amine to obtain 2-substituted quinoline;
 - b) reacting 2-substituted quinoline with boron tribromide (BBr_3) to get stable 2-(2-dibromoborylaryl) pyridines followed by further treating with trialkylaluminium (AlR_3) to obtain quinoline-borane complex of Formula (I).
- 20

In yet another embodiment, said metal catalyst is selected from Au(I), Chloro(triphenylphosphine)gold(I) (PPh_3AuCl) and silver triflate (AgOTf).

25 In still another embodiment, said suitable alkyne is selected from 2-ethynylbenzo[b]thiophene, 4-ethynyl-N,N-diphenylaniline, 1-ethynylpyrene, 9-(4-ethynylphenyl)-9H-carbazole, 9-ethynylphenanthrene, and 4-ethynyl-N,N-dimethylaniline.

In still another embodiment, said trialkylaluminium is selected from trimethylaluminium, triethylaluminium, trioctylaluminium, triphenylaluminium.

30 BRIEF DESCRIPTION OF THE DRAWINGS:

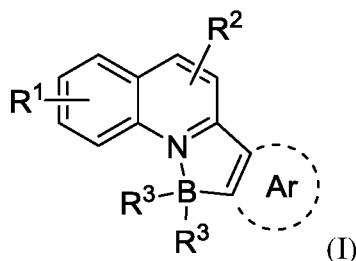
Fig 1: (a) depicts fluorescence spectra of compound 1a-6e in DCM and (b) depict fluorescence spectra of compound 1a-6e as powder.

Fig 2: (a) depicts solvatochromism of compound 2a in UV spectra and (b) depict solvatochromism of compound 2a in fluorescence spectra.

DETAILED DESCRIPTION OF THE INVENTION:

The invention will now be described in detail in connection with certain preferred and optional embodiments, so that various aspects thereof may be more fully understood and appreciated.

- 5 The present invention provides N,C-Chelate four-coordinate organoborons of Formula (I), wherein said organoborons exhibit tunable emission colours that cover the whole visible region, useful in bio imaging and in optoelectronic devices



wherein,

- 10 R^1 , R^2 and R^3 are selected independently from hydrogen, halogen, (un)substituted alkyl, (un)substituted aryl, (un)substituted heteroaryl, (un)substituted heterocyclic group; more particularly, R^1 , R^2 is H; R^3 is selected from methyl, ethyl, *n*-Octyl, phenyl.

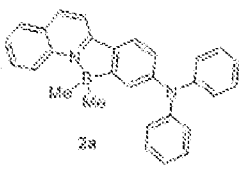
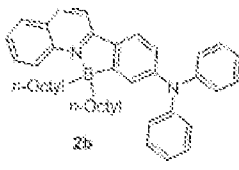
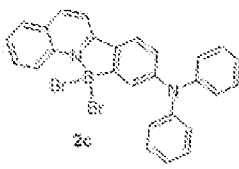
- 'ringAr' represent (un)substituted aryl, (un)substituted heteroaryl, (un)substituted heterocyclic group, more particularly, Ar is selected from benzo[thiophenyl, pyrenyl, phenanthrenyl, $Ph_2N-C_6H_4$, Carbazole- C_6H_4 , $Me_2N-C_6H_4$.
- 15

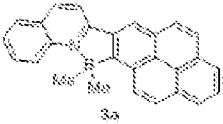
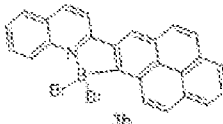
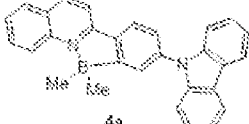
In an embodiment, the present invention provides N, C-Chelate four-coordinate organoborons of Formula (I) exhibit color tunability both in solid and solution state that can span the entire region of visible spectrum.

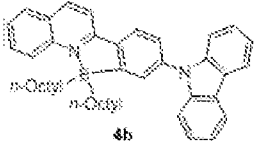
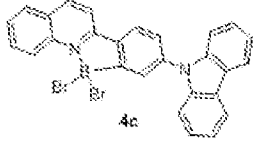
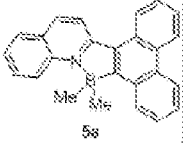
- 20 In another embodiment, the present invention provides novel full-color tunable light emitter based on N,C-chelate four-coordinate organoborons having excellent Quantum yield, stokes shift and solvate chromism of Formula (I).

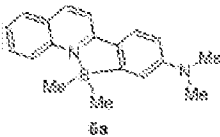
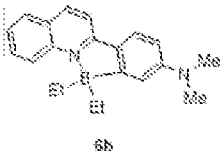
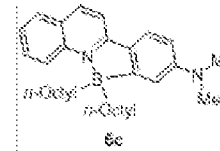
In an embodiment, the N, C-Chelate four-coordinate organoborons of Formula (I) and their spectral and physical data are given in Table 1 below:

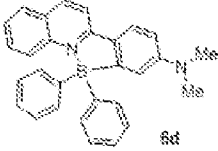
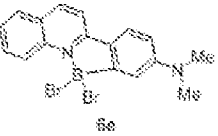
Compounds	Spectral and physical data
13 12,12-dimethyl-12H-12l4,13l4 benzo[4',5']thieno[3',2':3,4][1,2]azaborolo[1,5-a]quinoline	bluish solid, 91% yield; mp= 207-208°C; R_f = 0.55(Pet. ether/EtOAc = 80/20); 1H NMR (500MHz, $CDCl_3$) δ = 8.56 (d, J = 8.5 Hz, 1 H), 8.33 (d, J = 8.5 Hz, 1 H), 8.18 - 8.11 (m, 1 H), 7.99 - 7.94 (m, 1 H), 7.92 (d, J = 8.2 Hz, 1 H), 7.88 - 7.82 (m, 1 H), 7.71 (d, J = 8.5 Hz, 1 H), 7.57 (t, J = 7.5 Hz, 1 H), 7.48 - 7.37 (m, 2

	H), 0.43 (s, 6 H); ¹³ C NMR (126MHz , CDCl ₃) δ= 154.5, 146.5, 142.5, 140.6, 140.5, 133.4, 131.6, 129.0, 126.5, 126.4, 126.0, 125.8, 124.5, 123.4, 122.3, 116.6, 8.9; HRMS (ESI) calcd for C ₁₉ H ₁₇ NBS (M ⁺ + H) 302.1169, found 302.1169.
 2a 11,11-dimethyl-N,N-diphenyl-11H-1114,1214-benzo[3,4][1,2]azaborolo[1,5-a]quinolin-9-amine	greenish yellow solid, 90% yield; mp= 168-169°C; <i>R_f</i>= 0.60(Pet. ether/EtOAc = 80/20); ¹H NMR (400MHz , CDCl₃) δ = 8.66 - 8.56 (m, 1 H), 8.31 (d, <i>J</i> = 8.8 Hz, 1 H), 7.99 - 7.89 (m, 2 H), 7.87 - 7.78 (m, 2 H), 7.64 - 7.54 (m, 1 H), 7.45 (dd, <i>J</i> = 3.7, 5.9 Hz, 1 H), 7.42 - 7.33 (m, 4 H), 7.33 - 7.26 (m, 4 H), 7.21 - 7.12 (m, 2 H), 7.07 - 6.96 (m, 1 H), 0.32 (br. s., 6 H); ¹³C NMR (101MHz , CDCl₃) δ = 157.2, 150.5, 147.6, 142.1, 139.8, 131.1, 129.4, 129.3, 128.7, 127.0, 125.7, 125.4, 125.3, 123.4, 123.3, 123.0, 121.4, 119.7, 115.5, 9.2; HRMS (ESI) calcd for C₂₉H₂₆N₂B (M⁺+ H) 413.2184, found 413.2179.
 2b 11,11-dioctyl-N,N-diphenyl-11H-1114,1214-benzo[3,4][1,2]azaborolo[1,5-a]quinolin-9-amine	yellow solid, 56% yield; mp= 155-156°C <i>R_f</i>= 0.70(Pet. ether/EtOAc = 90/10); ¹H NMR (400MHz , CDCl₃) δ= 8.52 (d, <i>J</i> = 8.8 Hz, 1 H), 8.30 (d, <i>J</i> = 8.6 Hz, 1 H), 7.90 (d, <i>J</i> = 8.1 Hz, 1 H), 7.93 (d, <i>J</i> = 8.6 Hz, 1 H), 7.81 - 7.76 (m, 2 H), 7.56 (d, <i>J</i> = 7.3 Hz, 1 H), 7.39 (s, 1 H), 7.29 (d, <i>J</i> = 7.6 Hz, 5 H), 7.22 (s, 4 H), 7.09 (d, <i>J</i> = 7.1 Hz, 2 H), 6.96 (d, <i>J</i> = 8.3 Hz, 1 H), 1.43 (br. s., 2 H), 1.35 (s, 2 H), 1.30 (br. s., 13 H), 1.04 - 0.79 (m, 10 H), 0.29 (t, <i>J</i> = 7.6 Hz, 6 H); ¹³C NMR (101MHz , CDCl₃) δ= 158.3, 150.0, 147.7, 142.3, 139.7, 131.2, 129.4, 129.2, 128.7, 125.8, 125.1, 123.2, 123.0, 122.6, 122.4, 120.1, 115.3, 113.2, 31.9, 31.4, 30.2, 29.7, 29.4, 22.7, 17.1, 14.1, 14.1, 10.0; HRMS (ESI) calcd for C₄₃H₅₄N₂B (M⁺+ H) 609.4153, found 609.4155.
 2c 11,11-dibromo-N,N-diphenyl-11H-1114,1214-benzo[3,4][1,2]azaborolo[1,5-a]quinolin-9-amine	red solid, 95% yield; mp= 289-290°C; <i>R_f</i>= 0.30(DCM/MeOH = 95/05); ¹H NMR (400MHz , CD₂Cl₂) δ-d₂ = 9.10 - 9.01 (m, 1 H), 8.50 (d, <i>J</i> = 8.8 Hz, 1 H), 7.98 (d, <i>J</i> = 7.3 Hz, 2 H), 7.86 (d, <i>J</i> = 8.6 Hz, 1 H), 7.71 (d, <i>J</i> = 8.6 Hz, 1 H), 7.68 - 7.60 (m, 1 H), 7.43 - 7.32 (m, 5 H), 7.26 - 7.17 (m, 6 H), 6.98 (dd, <i>J</i> = 2.4, 8.6 Hz, 1 H); ¹³C NMR (101MHz , CD₂Cl₂) δ-d₂ □ = 147.1, 145.2, 132.9, 130.3, 129.7, 128.3,

	127.7, 127.0, 126.3, 125.5, 124.9, 123.9, 121.2, 120.6, 115.8; HRMS (ESI) calcd for $C_{27}H_{20}N_2BBr_2$ ($M^+ + H$) 543.0060, found 543.0061.
 14,14-dimethyl-14H-13l4,14l4-pyreno[1',2':3,4][1,2]azaborolo[1,5-a]quinolone	dark yellow solid, 86% yield; mp= 192-193°C; R_f = 0.62 (Pet. ether/EtOAc = 80/20); 1H NMR (400MHz, $CDCl_3$) δ = 9.03 (d, J = 9.3 Hz, 1 H), 8.94 (d, J = 9.0 Hz, 1 H), 8.83 (d, J = 9.3 Hz, 1 H), 8.55 - 8.46 (m, 2 H), 8.29 (d, J = 9.5 Hz, 1 H), 8.23 (dd, J = 5.9, 7.3 Hz, 2 H), 8.19 - 8.10 (m, 2 H), 8.05 - 7.97 (m, 2 H), 7.95 - 7.88 (m, 1 H), 7.69 - 7.60 (m, 1 H), 0.47 (s, 6 H); ^{13}C NMR (101MHz, $CDCl_3$) δ = 147.4, 140.2, 131.4, 129.9, 128.7, 128.7, 128.5, 128.3, 128.2, 127.0, 126.5, 126.0, 125.5, 125.4, 125.3, 123.8, 122.1, 119.8, 1.0; HRMS (ESI) calcd for $C_{27}H_{21}N_2B$ ($M^+ + H$) 370.1785, found 370.1785.
 14,14-dibromo-14H-13l4,14l4-pyreno[1',2':3,4][1,2]azaborolo[1,5-a]quinolone	reddish solid, 85% yield; mp = 155-156°C; R_f = 0.85 (Pet. ether/EtOAc = 90/10); 1H NMR (500MHz, $CDCl_3$) δ = 8.49 - 8.37 (m, 2 H), 8.31 - 8.24 (m, 2 H), 8.24 - 8.17 (m, 2 H), 7.98 - 7.93 (m, 1 H), 7.91 - 7.86 (m, 1 H), 7.84 - 7.73 (m, 3 H), 7.62 - 7.53 (m, 3 H), 7.52 - 7.45 (m, 2 H), 7.41 - 7.32 (m, 2 H); ^{13}C NMR (126MHz, $CDCl_3$) δ = 156.3, 148.3, 140.6, 138.6, 138.5, 136.9, 129.8, 129.7, 129.3, 129.0, 127.5, 127.2, 126.4, 126.0, 123.5, 120.3, 120.1, 118.7, 113.1, 109.8; HRMS (ESI) calcd for $C_{25}H_{20}O_2N_2F_3$ ($M^+ + H$) 437.1471, found 437.1469.
 9-(9H-carbazol-9-yl)-11,11-dimethyl-11H-11l4,12l4-benzo[3,4][1,2]azaborolo[1,5-a]quinoline	yellow solid, 88% yield; mp= 201-202°C; R_f = 0.56 (Pet. ether/EtOAc = 80/20); 1H NMR (400MHz, $CDCl_3$) δ = 8.70 (d, J = 8.8 Hz, 1 H), 8.44 (d, J = 8.6 Hz, 1 H), 8.17 (d, J = 8.1 Hz, 1 H), 8.20 (d, J = 7.6 Hz, 2 H), 8.12 (d, J = 8.8 Hz, 1 H), 8.01 - 7.95 (m, 2 H), 7.90 (ddd, J = 1.6, 7.0, 8.7 Hz, 1 H), 7.69 - 7.62 (m, 3 H), 7.56 (dd, J = 2.0, 8.1 Hz, 1 H), 7.51 - 7.43 (m, 2 H), 7.37 - 7.30 (m, 2 H), 0.39 (s, 6 H); ^{13}C NMR (101MHz, $CDCl_3$) δ = 156.9, 142.1, 140.7, 140.6, 139.9, 134.1, 131.5, 128.9, 127.6, 126.6, 125.9, 123.6, 123.6, 123.5, 123.4, 120.2, 120.0, 115.7, 110.3, 9.1; HRMS (ESI) calcd for $C_{29}H_{24}N_2B$ ($M^+ + H$) 411.2027, found 411.2028

 4b 9-(9H-carbazol-9-yl)-11,11-dioctyl-11H-11,12,14-benzo[3,4][1,2]azaborolo[1,5-a]quinoline	yellow solid, 55% yield; mp= 188-189°C; R_f = 0.72(Pet. ether/EtOAc = 90/10); $^1\text{H NMR}$ (400MHz, CDCl_3) δ = 8.68 (d, J = 8.8 Hz, 1 H), 8.45 (d, J = 8.8 Hz, 1 H), 8.21 (d, J = 7.8 Hz, 3 H), 8.14 (d, J = 8.8 Hz, 1 H), 7.99 (d, J = 8.1 Hz, 1 H), 7.96 - 7.93 (m, 1 H), 7.90 (d, J = 8.3 Hz, 1 H), 7.68 - 7.64 (m, 1 H), 7.62 (d, J = 8.1 Hz, 2 H), 7.58 - 7.55 (m, 1 H), 7.49 (d, J = 7.1 Hz, 2 H), 7.34 (t, J = 7.3 Hz, 2 H), 1.37 (br. s., 2 H), 1.29 (s, 11 H), 1.24 (br. s., 1 H), 1.16 (dd, J = 7.7, 13.8 Hz, 4 H), 1.03 (dd, J = 7.5, 13.8 Hz, 4 H), 0.96 - 0.79 (m, 6 H), 0.40 (t, J = 7.6 Hz, 6 H); $^{13}\text{C NMR}$ (101MHz, CDCl_3) δ = 157.9, 142.3, 140.8, 140.5, 139.4, 137.1, 135.5, 131.6, 129.9, 129.7, 129.1, 128.9, 127.5, 127.4, 127.3, 127.0, 126.6, 126.0, 125.9, 123.6, 123.4, 122.8, 120.4, 120.3, 120.1, 119.9, 118.8, 115.5, 110.2, 109.9, 31.9, 29.7, 29.4, 22.7, 17.1, 17.0, 14.1, 10.1; HRMS (ESI) calcd for $\text{C}_{43}\text{H}_{52}\text{N}_2\text{B}$ (M^+ + H) 607.4153, found 607.4155.
 4c 11,11-dibromo-9-(9H-carbazol-9-yl)-11H-11,12,14-benzo[3,4][1,2]azaborolo[1,5-a]quinoline	orange solid, 88% yield; mp= 231-232°C; R_f = 0.40(DCM/MeOH = 95/05); $^1\text{H NMR}$ (400MHz, CDCl_3) δ = 8.45 - 8.39 (m, 2 H), 8.32 (d, J = 8.6 Hz, 1 H), 8.24 (d, J = 8.6 Hz, 1 H), 8.18 (d, J = 7.8 Hz, 2 H), 7.99 (d, J = 8.6 Hz, 1 H), 7.90 (dd, J = 1.5, 8.3 Hz, 1 H), 7.81 - 7.75 (m, 3 H), 7.61 - 7.56 (m, 1 H), 7.53 (d, J = 8.1 Hz, 2 H), 7.47 - 7.44 (m, 2 H), 7.34 (d, J = 6.8 Hz, 2 H), 7.23 - 7.19 (m, 1 H), 6.77 (t, J = 7.5 Hz, 1 H), 6.68 - 6.64 (m, 1 H); $^{13}\text{C NMR}$ (101MHz, CDCl_3) δ = 137.1, 129.9, 129.7, 129.4, 129.1, 127.5, 127.3, 126.5, 126.2, 126.0, 123.5, 120.3, 120.1, 118.9, 113.3, 109.8; HRMS (ESI) calcd for $\text{C}_{27}\text{H}_{18}\text{N}_2\text{BB}^{81}\text{Br}$ (M^+ + H) 540.9904, found 540.9903.
 5a 9,9-dimethyl-9H-9,10,14-phenanthro[9',10':3,4][1,2]azaborolo[1,5-a]quinoline	bluish green solid, 85% yield; mp= 242-243°C; R_f = 0.80(Pet. ether/EtOAc = 90/10); $^1\text{H NMR}$ (500MHz, CDCl_3) δ = 8.86 (td, J = 0.8, 8.2 Hz, 1 H), 8.81 - 8.77 (m, 2 H), 8.77 - 8.74 (m, 1 H), 8.72 (d, J = 8.9 Hz, 1 H), 8.64 (dd, J = 2.0, 7.5 Hz, 1 H), 8.41 (d, J = 8.9 Hz, 1 H), 7.96 - 7.92 (m, 1 H), 7.88 (ddd, J = 1.7, 6.9, 8.8 Hz, 1 H), 7.79 - 7.69 (m, 3 H), 7.68 - 7.64 (m, 1 H), 7.60 (t, J = 7.5 Hz, 1 H), 0.59 (s, 6 H);

	¹³ C NMR (126MHz , CDCl ₃) δ = 158.4, 142.0, 140.0, 131.2, 131.1, 128.8, 128.2, 126.9, 126.7, 126.6, 126.5, 125.0, 124.0, 123.3, 123.2, 123.0, 122.6, 119.1, 10.9; HRMS (ESI) calcd for C ₂₅ H ₂₁ NB (M ⁺ + H) 346.1762, found 346.1762.
 N,N,11,11-tetramethyl-11H-1114,1214-benzo[3,4][1,2]azaborolo[1,5-a]quinolin-9-amine	yellow solid, 88% yield; mp= 154-156°C; <i>R_f</i>= 0.62(Pet. ether/EtOAc = 80/20); ¹H NMR (400MHz , CDCl₃) δ = 8.54 (d, <i>J</i> = 8.6 Hz, 1 H), 8.17 (d, <i>J</i> = 8.8 Hz, 1 H), 7.89 - 7.80 (m, 3 H), 7.80 - 7.72 (m, 1 H), 7.48 (t, <i>J</i> = 7.6 Hz, 1 H), 7.05 - 6.94 (m, 1 H), 6.73 - 6.65 (m, 1 H), 3.14 (s, 6 H), 0.41 - 0.21 (m, 6 H); ¹³C NMR (101MHz , CDCl₃) δ = 157.8, 152.4, 142.2, 139.3, 130.8, 128.7, 126.6, 124.9, 124.5, 123.9, 122.5, 115.4, 110.4, 109.9, 40.4, 9.54; HRMS (ESI) calcd for C₁₉H₂₂N₂B (M⁺+ H) 289.1871, found 289.1871.
 11,11-diethyl-N,N-dimethyl-11H-1114,1214-benzo[3,4][1,2]azaborolo[1,5-a]quinolin-9-amine	yellow solid, 88% yield; mp= 154-156°C; <i>R_f</i>= 0.70(Pet. ether/EtOAc = 90/10); ¹H NMR (400MHz , CDCl₃) δ= 8.47 (d, <i>J</i> = 8.8 Hz, 1 H), 8.20 (d, <i>J</i> = 8.8 Hz, 1 H), 7.93 - 7.79 (m, 3 H), 7.74 (ddd, <i>J</i> = 1.6, 7.0, 8.7 Hz, 1 H), 7.55 - 7.43 (m, 1 H), 6.95 (d, <i>J</i> = 2.7 Hz, 1 H), 6.69 (dd, <i>J</i> = 2.4, 8.6 Hz, 1 H), 3.13 (s, 6 H), 1.02 - 0.86 (m, 4 H), 0.40 - 0.26 (m, 6 H); ¹³C NMR (101MHz , CDCl₃) δ= 159.0, 152.1, 142.5, 139.2, 130.9, 128.6, 126.3, 126.2, 125.0, 123.5, 122.0, 115.2, 111.0, 109.7 , 40.4, 9.9; HRMS (ESI) calcd for C₂₁H₂₆N₂B (M⁺+ H) 317.2184, found 317.2182.
 N,N-dimethyl-11,11-dioctyl-11H-1114,1214-benzo[3,4][1,2]azaborolo[1,5-a]quinolin-9-amine	yellow solid, 55% yield; mp= 176-177°C <i>R_f</i>= 0.75(Pet. ether/EtOAc = 90/10); ¹H NMR (400MHz , CDCl₃) δ = 8.48 (d, <i>J</i> = 8.8 Hz, 1 H), 8.20 (d, <i>J</i> = 8.8 Hz, 1 H), 7.88 - 7.79 (m, 3 H), 7.78 - 7.70 (m, 1 H), 7.48 (t, <i>J</i> = 7.5 Hz, 1 H), 6.96 (dd, <i>J</i> = 0.5, 2.2 Hz, 1 H), 6.69 (dd, <i>J</i> = 2.4, 8.6 Hz, 1 H), 3.14 (s, 6 H), 1.34 - 1.21 (m, 14 H), 1.07 - 0.77 (m, 14 H), 0.33 (t, <i>J</i> = 7.7 Hz, 6 H); ¹³C NMR (101MHz , CDCl₃) δ = 158.9, 152.0, 142.4, 139.2, 130.9, 128.6, 126.3, 126.2, 125.0, 123.5, 122.0, 115.2, 111.0, 109.7, 40.4, 31.9, 29.7, 29.6, 29.4, 22.7, 14.1, 9.9; HRMS (ESI) calcd for C₃₃H₅₀N₂B (M⁺+ H) 485.4095, found 485.4097.

 N,N-dimethyl-11,11-diphenyl-11H-1114,1214-benzo[3,4][1,2]azaborolo[1,5-a]quinolin-9-amine	orange solid, 46% yield; mp= 289-290°C; R_f= 0.62(Pet. ether/EtOAc = 80/20); $^1\text{H NMR}$ (400MHz, CDCl_3) δ = 8.31 (d, J = 8.6 Hz, 1 H), 8.00 - 7.94 (m, 2 H), 7.85 - 7.77 (m, 2 H), 7.55 (d, J = 8.6 Hz, 1 H), 7.34 (td, J = 1.2, 7.5 Hz, 5 H), 7.19 - 7.14 (m, 4 H), 7.12 - 7.08 (m, 2 H), 6.91 (d, J = 2.4 Hz, 1 H), 6.62 (s, 1 H), 3.01 (s, 6 H); $^{13}\text{C NMR}$ (126MHz, CDCl_3) δ = 160.2, 153.1, 142.0, 140.7, 139.3, 133.5, 131.1, 128.4, 127.1, 126.6, 125.3, 125.0, 124.5, 124.0, 123.7, 119.1, 115.4, 114.1, 111.7, 110.2, 40.3; HRMS (ESI) calcd for $\text{C}_{29}\text{H}_{26}\text{N}_2\text{B}$ ($\text{M}^+ + \text{H}$) 413.2117, found 413.2114.
 11,11-dibromo-N,N-dimethyl-11H-1114,1214-benzo[3,4][1,2]azaborolo[1,5-a]quinolin-9-amine	red solid, 91% yield; mp= 168-169°C; R_f= 0.32(DCM/MeOH = 95/05); $^1\text{H NMR}$ (500MHz, CD_2Cl_2) δ -d_2) = 8.16 - 8.10 (m, 3 H), 7.86 (d, J = 8.5 Hz, 1 H), 7.80 (d, J = 7.6 Hz, 1 H), 7.69 (t, J = 7.2 Hz, 1 H), 7.51 - 7.42 (m, 1 H), 6.83 (d, J = 7.9 Hz, 2 H), 3.05 (br. s., 6 H); $^{13}\text{C NMR}$ (126MHz, CD_2Cl_2) δ -d_2) = 157.3, 152.2, 148.2, 144.4, 137.2, 132.5, 130.2, 129.1, 129.0, 128.0, 127.2, 126.0, 118.6, 112.5, 112.2, 40.6; HRMS (ESI) calcd for $\text{C}_{17}\text{H}_{16}\text{N}_2\text{BBr}^{81}\text{Br}$ ($\text{M}^+ + \text{H}$) 418.9747, found 418.9745.

In still another embodiment, the present invention provides a process for synthesis of N, C-Chelate four-coordinate organoborons of Formula (I) comprising the steps of:

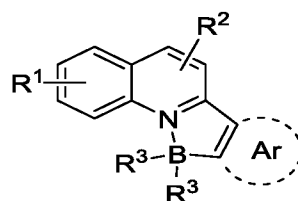
- a) reacting 2-amino benzaldehyde with suitable alkyne in presence of metal as catalyst and an amine to obtain 2-substituted quinoline;
- b) reacting 2-substituted quinoline with boron tribromide (BBr_3) to get stable 2-(2-dibromoborylaryl) pyridines followed by further treating with trialkylaluminium (AlR_3) to obtain quinoline-borane complex of Formula (I).

In yet another embodiment, said metalcatalyst is selected from Au(I), Chloro(triphenylphosphine)gold(I) (PPh_3AuCl), silver triflate (AgOTf).

In still another embodiment, said suitable alkyne is selected from 2-ethynylbenzo[b]thiophene, 4-ethynyl-N,N-diphenylaniline, 1-ethynylpyrene, 9-(4-ethynylphenyl)-9H-carbazole, 9-ethynylphenanthrene, 4-ethynyl-N,N-dimethylaniline.

In still another embodiment, saidtrialkylaluminium is selected from
5 trimethylaluminium, triethylaluminium, trioctylaluminium, triphenylaluminium.

In further embodiment, the present invention provides a novel full-color tunable light emitter based on N,C-chelate four-coordinate organoborons having excellent Quantum yield, stokes shift, fluorescent lifetimeand solvate chromism of Formula (I)



(I)

wherein,

R^1 , R^2 and R^3 are selected independently from hydrogen, halogen, (un)substituted alkyl, (un)substituted aryl, (un)substituted heteroaryl, (un)substituted heterocyclic group; said R^1 , R^2 is selected from hydrogen, R^3 is selected from Methyl, Ethyl,
15 "Octyl, Phenyl;

'ringAr' represent (un)substituted aryl, (un)substituted heteroaryl, (un)substituted heterocyclic group; said Ar is selected from Benzothiophenyl, Pyrenyl, Phenathrenyl, $Ph_2N-C_6H_4$, Carbazole- C_6H_4 , $Me_2N-C_6H_4$;

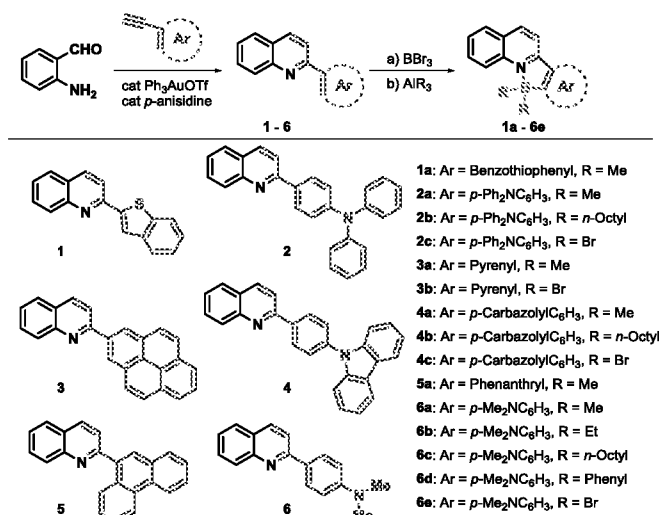
said Quantum yield is ranging from 0.9 to 0.81;

20 saidstokes shift is in solid state ranging from 93 to 197 and in solution state ranging from 60 to 165; and

said fluorescent lifetime is ranging from 2.1 to 6.9.

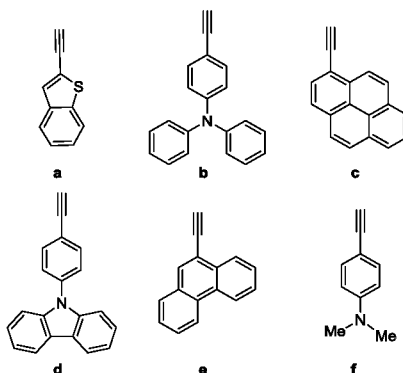
The process is as shown in Scheme 1 below:

25



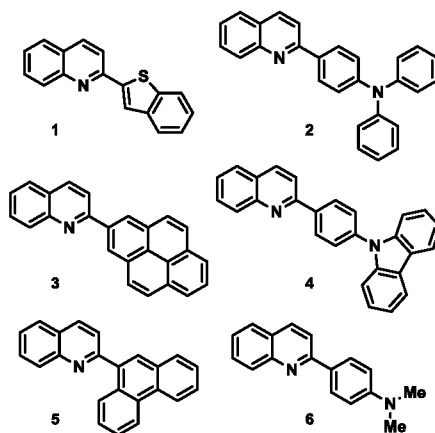
Scheme 1

The terminal alkynes used in the process are prepared according to known procedure and comprises the following:



B. Blanco, A. Sedes, A. Peón, H. Lamb, A. R. Hawkins, L. Castedoc, C. González-Bello, *Org. Biomol. Chem.*, 2012, **10**, 3662; M. Planells, A. Abate, D. J. Hollman, S. D. Stranks, V. Bharti, J. Gaur, D. Mohanty, S. Chand, H. J. Snaith, N. Robertson, *J. Mater. Chem. A*, 2013, **1**, 6949; V. V. Filichev, I. V. Astakhova, A. D. Malakhov, V. A. Korshun, E. B. Pedersen, *Chem. Eur. J.*, 2008, **14**, 9968; M. Hayashi, R. Sakamoto, H. Nishihara, *Chem. Eur. J.*, 2012, **18**, 8610; S. Grunder, D. M. Torres, C. Marquardt, A. Blaszczyk, R. Krupke, M. Mayor, *Eur. J. Org. Chem.*, 2011, 478-496; R. C. Lirag, Ha T. M. Le, O. Š. Miljanić, *Chem. Commun.*, 2013, **49**, 4304.

The 2-substituted quinolines (1-6) prepared by step (a) comprises;



The intermediate 2-(2-dibromoborylaryl)pyridines are stable enough to be handled in air and serve as the synthetic platform for variously substituted pyridine–borane complexes.

- 5 The N, C-chelate four-coordinate organoborons derivatives (Formula I) produced are stable in air and water, have high thermal stability as indicated by TGA.

In preferred embodiment, the compounds of general Formula (I) (i.e. 1a to 6e) show intense fluorescence both in solution and solid state. The compounds exhibited broad absorption band between 387- 491 nm with regards to the electronic transition originating from the π -molecular orbitals. The fluorescence spectra of complexes 1a–6e in both solution and the solid state were recorded and shown in Fig. 1a and 1b. The fluorophores exhibited intense emission in CH_2Cl_2 solutions when excited at their absorption maxima. The emission profiles of these compounds in solution, having emission bands that peaked at 466 nm (1a) to 637 nm (2c), covering a wide range from blue to red, reflected that the substituent at the 2nd position of quinoline was effective in tuning the emission color of this type of N, C-chelate four-coordinate organoborons.

Further, the solid-state fluorescence spectra of the compounds in powder forms are measured and are shown in Fig. 1a and 1b. The fluorescence of the solid samples with emission peaks at 491 nm (for 1a) and 670 nm (for 6e) also covered a wide range from blue to deep red. The emission maxima of complexes 1a – 6a in solid state shows blue and red shifted compared with those of solution state which reflected crystallochromy effects. This indicates that all the solid samples are highly emissive with excellent quantum yields. The absolute fluorescence quantum yields of solutions were calculated using an integrating sphere method. The methyl group substituted on boron atom compounds showed good quantum yield (ϕ_f 0.81 for 3a) compared to bromo substituent (ϕ_f 0.03 for 2c).

The photophysical data for compounds 1a-6e including Stokes shift, quantum yields, and fluorescence lifetime are given in Table 2 below:

Table 2: Photophysical data for compounds 1a-6e

Compound	Δ Stokes (nm) ^a		ϕ_f^b	τ_f (ns) ^f
	solution	solid	CH ₂ Cl ₂	
1a	060	098	0.58	5.2
2a	113	118	0.56	6.4
2b	114	115	0.60	6.0
2c	146	165	0.03	2.1
3a	073	194	0.81	4.0
3b	080	188	0.60	4.8
4a	110	093	0.71	6.2
4b	105	097	0.67	6.1
4c	165	197	0.09	3.2
5a	058	106	0.78	5.5
6a	098	149	0.50	6.6
6b	099	142	0.59	6.2
6c	101	133	0.58	6.9
6d	097	117	0.43	6.9
6e	102	180	0.14	2.5

^aStokes shift= $\lambda_{em}-\lambda_{abs}$; ^eQuantum yields; ^ffluorescent lifetime

5 In another embodiment, the compounds N, C-chelate four-coordinate organoborons also showed positive solvatochromic behaviour as emission wavelengths are found to be red shifted with increase in solvent polarity (Figure 2).

The electrochemical properties of N, C-chelate four-coordinate organoborons (Formula I) were investigated by cyclic voltammetry (CV). All luminogens exhibited similar CV curves with two irreversible oxidation peaks. The low LUMO value of N, C-chelate four-coordinate organoborons was comparable to those of silole derivatives (e.g., -2.77 and -2.81 eV), indicating that BNC (boron, nitrogen and carbon) is a potential electron transporter. The electrochemical properties are given in Table 3.

15 **Table 3: Electrochemical properties of compounds of 1a to 6e:**

Sr.No	Compound	λ_{exc} (nm) ^[a]	E _{onset}	HOMO	LUMO	Δ (eV) ^[d]
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				(ev) ^[b]	(ev) ^[c]	
1	1a	433	1.03	-5.43	-2.57	2.86
2	2a	480	0.58	-4.98	-2.40	2.58
3	2c	544	0.65	-5.05	-2.78	2.27
4	3a	453	1.19	-5.59	-2.86	2.73
5	3b	496	1.13	-5.53	-3.03	2.50
6	4a	431	0.93	-5.33	-2.46	2.87
7	4c	495	1.06	-5.46	-2.96	2.50
8	5a	431	1.02	-5.42	-2.55	2.87
9	6a	483	0.47	-4.87	-2.31	2.56
10	6e	540	1.01	-5.41	-3.12	2.29

^[a] wavelength estimated from the onset of absorption spectrum; ^[b] HOMO = -(4.4+E_{onset})

^[c] LUMO= -(HOMO + Eg); ^[d] the energy gap between the HOMO and LUMO

In yet another embodiment, the present invention relates to the use of N, C-chelate
 5 four-coordinate organoborons for *in vitro* bio-imaging and in optoelectronic devices.

The following examples, which include preferred embodiments, will serve to illustrate the practice of this invention, it being understood that the particulars shown are by way of example and for purpose of illustrative discussion of preferred embodiments of the invention.

10 **Example 1: General procedure preparation of alkynes:**

The terminal alkynes a, b, c, d, e and f are prepared according to literature known procedure.

a) Synthesis of trimethyl(phenylethynyl)silane derivatives :

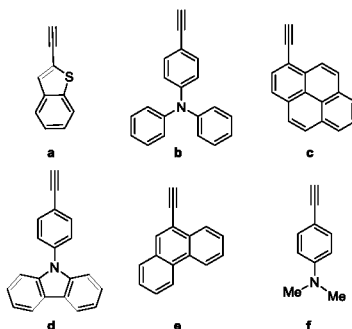
To a solution of Aryl bromide/iodide derivatives (25 mmol), CuI (1.0 mmol, 190 mg) and
 15 Pd(PPh₃)₂Cl₂ (0.5 mmol, 350 mg) in dried THF (25 ml) was added triethylamine (50 mmol, 5.0 g). A solution of trimethylsilylacetylene (37.5 mmol, in 5.0 ml of THF) was then added dropwise via syringe under nitrogen. The resulting solution was stirred at room temperature for 12 h. The reaction mixture was filtered through Celite and the solvent was removed by rotary evaporation. The residue was treated with water and extracted with ethyl ether. The
 20 combined organic layer was washed with brine and dried over magnesium sulfate. After the removal of solvent, the crude product was purified with silica gel column chromatography (ethyl acetate/petroleum ether, v/v = 1/100) affording pure trimethyl(phenyl ethynyl)silane derivatives).

25 **2) Synthesis of Aryl acetylene derivatives via desilylation reactions:**

To a solution of trimethyl(phenylethynyl)silane derivatives (10 mmol) in methanol (20 ml) and CH₂Cl₂ (10 ml) (v/v = 2:1) was added K₂CO₃ (30 mmol, 4.2 g) and stirred at

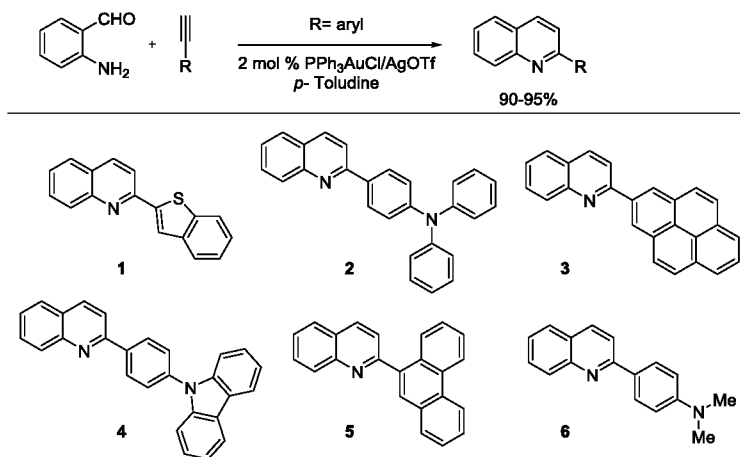
RT for 12 h. The resulting mixture was treated with water and extracted with ethyl ether. The combined organic layer was washed with brine and dried over magnesium sulfate. The solvent was removed and the residue was distilled carefully under reduced pressure or purified by silica gel column chromatography to afford the pure products.

5



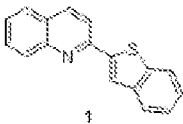
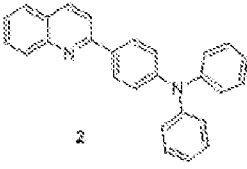
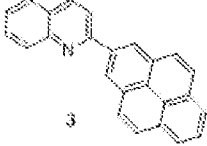
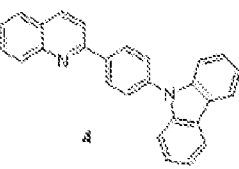
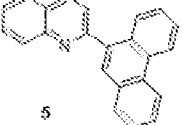
Example 2: General procedure for preparation of various 2 substituted quinolines (1-6)

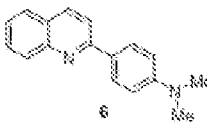
To a screw-cap vial containing stir bar, were added 2- amino-benzaldehydes (0.3 mmol), terminal alkynes (0.36 mmol, 1.2 equiv.), PPh_3AuCl (2 mol %), AgOTf (2 mol %), dry DCE (2 ml) and *p*-anisidine (25 mol %). The reaction vial was fitted with cap, evacuated and filled with nitrogen and heated at 100°C for 12 h. The reaction mixture was allowed to bring to ambient temperature. The reaction mixture was diluted with ethyl acetate and filtered through a plug of silica gel. The filtrate was concentrated under reduced pressure and the resulting residue was purified by column chromatography (silica gel, hexane/EtOAc) to give the desired 2 substituted quinolines.



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Table 4: The compounds 1-6 and their physical and spectral data are as follows:

compounds	Physical and spectral data
 1	light yellow solid, 88% yield; mp= 198-199°C; R_f = 0.90(Pet. ether/EtOAc = 90/10); $^1\text{H NMR}$ (400MHz, CDCl_3) δ = 8.21 - 8.14 (m, 2 H), 8.00 - 7.97 (m, 1 H), 7.96 - 7.90 (m, 2 H), 7.88 - 7.83 (m, 1 H), 7.82 - 7.78 (m, 1 H), 7.74 (ddd, J = 1.5, 6.8, 8.6 Hz, 1 H), 7.57 - 7.50 (m, 1 H), 7.43 - 7.36 (m, 2 H); $^{13}\text{C NMR}$ (101MHz, CDCl_3) δ = 152.2, 148.0, 145.4, 141.1, 140.4, 136.6, 129.9, 129.4, 127.5, 126.5, 125.3, 124.5, 124.3, 122.6, 122.4, 117.8, 113.2; HRMS (ESI) calcd for $\text{C}_{17}\text{H}_{12}\text{NS}$ (M^+ + H) 262.0685, found 262.0683.
 2	light yellow solid, 92% yield; mp= 162-163°C; R_f = 0.75(Pet. ether/EtOAc = 90/10); $^1\text{H NMR}$ (400MHz, CDCl_3) δ = 8.22 - 8.13 (m, 2 H), 8.11 - 8.02 (m, 2 H), 7.87 - 7.77 (m, 2 H), 7.76 - 7.69 (m, 1 H), 7.55 - 7.46 (m, 1 H), 7.36 - 7.28 (m, 4 H), 7.26 - 7.16 (m, 6 H), 7.13 - 7.05 (m, 2 H); $^{13}\text{C NMR}$ (101MHz, CDCl_3) δ = 156.9, 149.0, 148.3, 147.4, 136.6, 133.2, 129.5, 129.3, 128.4, 127.4, 126.9, 125.9, 124.8, 123.3, 123.1, 118.6; HRMS (ESI) calcd for $\text{C}_{27}\text{H}_{21}\text{N}_2$ (M^+ + H) 373.1699, found 373.1698.
 3	light yellow solid, 88% yield; mp= 148-149°C; R_f = 0.82(Pet. ether/EtOAc = 90/10); $^1\text{H NMR}$ (400MHz, CDCl_3) δ = 8.46 (d, J = 9.3 Hz, 1 H), 8.36 (d, J = 8.6 Hz, 1 H), 8.34 - 8.27 (m, 3 H), 8.26 - 8.19 (m, 2 H), 8.15 (s, 2 H), 8.10 (d, J = 9.3 Hz, 1 H), 8.08 - 8.01 (m, 1 H), 8.00 - 7.93 (m, 1 H), 7.88 (d, J = 8.3 Hz, 1 H), 7.83 (ddd, J = 1.5, 6.9, 8.5 Hz, 1 H), 7.68 - 7.61 (m, 1 H); $^{13}\text{C NMR}$ (101MHz, CDCl_3) δ = 159.7, 148.3, 136.2, 135.9, 131.6, 131.4, 130.9, 129.8, 129.8, 128.8, 128.2, 128.0, 127.7, 127.6, 127.4, 126.9, 126.6, 126.0, 125.4, 125.1, 124.9, 124.8, 123.8; HRMS (ESI) calcd for $\text{C}_{25}\text{H}_{16}\text{N}$ (M^+ + H) 330.1277, found 330.1277.
 4	light yellow solid, 82% yield; mp= 155-156°C; R_f = 0.85(Pet. ether/EtOAc = 90/10); $^1\text{H NMR}$ (500MHz, CDCl_3) δ = 8.49 - 8.37 (m, 2 H), 8.31 - 8.24 (m, 2 H), 8.24 - 8.17 (m, 2 H), 7.98 - 7.93 (m, 1 H), 7.91 - 7.86 (m, 1 H), 7.84 - 7.73 (m, 3 H), 7.62 - 7.53 (m, 3 H), 7.52 - 7.45 (m, 2 H), 7.41 - 7.32 (m, 2 H); $^{13}\text{C NMR}$ (126MHz, CDCl_3) δ = 156.3, 148.3, 140.6, 138.6, 138.5, 136.9, 129.8, 129.7, 129.3, 129.0, 127.5, 127.2, 126.4, 126.0, 123.5, 120.3, 120.1, 118.7, 113.1, 109.8; HRMS (ESI) calcd for $\text{C}_{27}\text{H}_{19}\text{N}_2$ (M^+ + H) 371.1543, found 371.1541.
 5	off white solid, 90% yield; mp= 118-119°C R_f = 0.88(Pet. ether/EtOAc = 90/10); $^1\text{H NMR}$ (500MHz, CDCl_3) δ = 8.82 (d, J = 8.2 Hz, 1 H), 8.77 (d, J = 8.2 Hz, 1 H), 8.32 (d, J = 8.2 Hz, 1 H), 8.28 (d, J = 8.5 Hz, 1 H), 8.15 - 8.09 (m, 1 H), 8.00 (s, 1 H), 7.99 - 7.97 (m, 1 H), 7.96 - 7.93 (m, 1 H), 7.82 (ddd, J = 1.7, 6.9, 8.5 Hz, 1 H), 7.77 (d, J = 8.2 Hz, 1 H), 7.75 - 7.68 (m, 2 H), 7.67 - 7.61 (m, 2 H), 7.58 (ddd, J = 1.4, 6.9, 8.2 Hz, 1 H); $^{13}\text{C NMR}$ (126MHz, CDCl_3) δ = 159.4, 148.1, 137.4, 136.3, 136.2, 131.3, 130.8, 130.5, 130.3, 129.8, 129.7, 129.1, 128.8, 128.5, 128.3, 127.6, 127.1, 126.8, 126.8, 126.7, 126.6, 126.1, 123.4, 123.3,

	123.0, 122.6; HRMS (ESI) calcd for C ₂₃ H ₁₆ N (M ⁺ + H) 306.1277, found 306.1278.
	off white solid, 86% yield; mp= 180-181°C <i>R</i> _f = 0.82(Pet. ether/EtOAc = 90/10); ¹H NMR (400MHz, CDCl₃) δ = 8.17 - 8.07 (m, 4 H), 7.84 (d, <i>J</i> = 8.6 Hz, 1 H), 7.80 - 7.75 (m, 1 H), 7.72 - 7.65 (m, 1 H), 7.49 - 7.41 (m, 1 H), 6.88 - 6.81 (m, 2 H), 3.06 (s, 6 H); ¹³C NMR (101MHz, CDCl₃) δ = 157.3, 151.3, 148.4, 136.2, 129.3, 128.4, 127.3, 126.7, 125.3, 118.3, 112.2, 40.3; HRMS (ESI) calcd for C ₁₇ H ₁₇ N ₂ (M ⁺ + H) 249.1386, found 249.1386.

Example 3: General procedure for Electrophilic Aromatic Borylation of 2-substituted quinolines.

To a stirred solution of 2- substituted quinolines (200 mg, 0.65 mmol) and *i*-Pr₂NEt (86 mg, 0.65 mmol) in CH₂Cl₂ (0.5 mL) at 0°C was added BBr₃ (1.0M in CH₂Cl₂ 2.0 mL, 1.9 mmol). After being stirred at room temperature for 24 h, saturated K₂CO₃ aqueous solution was added to the reaction mixture. The reaction was poured into water, the organic layer was separated and extracted with CH₂Cl₂ (twice), washed with water (once), brine (once), dried over Na₂SO₄ and concentrated. The resulting solid was collected by filtration and washed with hexane to give quinoline–borane complex (280 mg, 89% yield).

Example 4: General procedure for Bromine-alkyl group exchange with trialkyl-aluminium

To a stirred solution of quinoline–borane complex (200 mg, 0.35 mmol) in toluene/CH₂Cl₂ (1:1) at room temperature was added Me₃Al (1.1 M in hexane, 0.75 mL, 0.77 mmol). After being stirred at this temperature for 5 min, the reaction was quenched by adding water. The organic layer was separated and extracted with CH₂Cl₂ (twice), washed with water (once), brine (once), and dried over MgSO₄ and concentrated. After filtration and solvent evaporation, the residue was purified by silica-gel column chromatography by using hexane/EtOAc mixture as eluent. A pale yellow solid was obtained in 91% yield to afford product.

The compounds 1a to 6e prepared by the above process was characterized by UV-vis absorption and fluorescence spectra both in solution (DCM) and in solid state (Fig. 1a and 1b).

Example 5: Calculation of Quantum yields:

The absolute fluorescence quantum yields of solutions were calculated using an integrating sphere method. The methyl group substituted on boron atom compounds showed good quantum yield (φ_f 0.81 for 3a) compare to bromo substituent (φ_f 0.03 for 2c).

Example 6: Measurement of Fluorescence Lifetime

The Fluorescence lifetime for all organoboranes 1a - 6e were measured in CH₂Cl₂ upon excitation at 431 nm and 591 nm. Data were taken at 431, 591 and emission peak of each compound. All compounds showed more or less similar lifetime values ranging in
5 between 2.5-6.9 ns.

The photophysical data for compounds 1a-6e including Stokes shift, quantum yields, and fluorescence lifetime are given in Table 5 below:

Compound	Δ Stokes (nm) ^a		ϕ_f^b	τ_f (ns) ^f
	solution	solid	CH ₂ Cl ₂	
1a	060	098	0.58	5.2
2a	113	118	0.56	6.4
2b	114	115	0.60	6.0
2c	146	165	0.03	2.1
3a	073	194	0.81	4.0
3b	080	188	0.60	4.8
4a	110	093	0.71	6.2
4b	105	097	0.67	6.1
4c	165	197	0.09	3.2
5a	058	106	0.78	5.5
6a	098	149	0.50	6.6
6b	099	142	0.59	6.2
6c	101	133	0.58	6.9
6d	097	117	0.43	6.9
6e	102	180	0.14	2.5

^cStokes shift= $\lambda_{em}-\lambda_{abs}$; ^eQuantum yields; ^ffluorescent lifetime

Example 7: Cyclic voltammetry

The electrochemical properties of N, C-chelate four-coordinate organoborons were investigated by cyclic voltammetry (CV). All luminogens exhibited similar CV curves with two irreversible oxidation peaks. The oxidation onset potentials (E_{onset}) of N, C-chelate four-coordinate organoborons occur between 0.47 to 1.19 V, from which the HOMO energy levels were determined to be -4.87 to -5.59 eV (HOMO = -(4.4 + E_{onset})). Their
10 LUMO energy levels can be obtained from the optical band gap energies (E_g) and the HOMO values (LUMO = -(HOMO + E_g), and are located between -2.77 to -2.81 eV. The
15

low LUMO value of N, C-chelate four-coordinate organoborons is comparable to those of silole derivatives (e.g., -2.77 and -2.81 eV), indicating that BNC is a potential electron transporter.

Table 6: Electrochemical properties of compounds of 1a to 6e:

Sr.No	Compound	$\lambda_{\text{exc}} (\text{nm})^{[a]}$	E_{onset}	HOMO (ev) ^[b]	LUMO (ev) ^[c]	$\Delta (\text{ev})^{[d]}$
1	1a	433	1.03	-5.43	-2.57	2.86
2	2a	480	0.58	-4.98	-2.40	2.58
3	2c	544	0.65	-5.05	-2.78	2.27
4	3a	453	1.19	-5.59	-2.86	2.73
5	3b	496	1.13	-5.53	-3.03	2.50
6	4a	431	0.93	-5.33	-2.46	2.87
7	4c	495	1.06	-5.46	-2.96	2.50
8	5a	431	1.02	-5.42	-2.55	2.87
9	6a	483	0.47	-4.87	-2.31	2.56
10	6e	540	1.01	-5.41	-3.12	2.29

^[a] wavelength estimated from the onset of absorption spectrum; ^[b] HOMO = -(4.4+E_{onset})
^[c] LUMO= -(HOMO + E_g); ^[d] the energy gap between the HOMO and LUMO

Example 8: X-ray Crystallography Data

X-ray intensity data measurements of compounds **2a**, **3a**, **4a**, **5a**, and **6b** were carried out on a Bruker SMART APEX II CCD diffractometer with graphite-monochromatized (MoK α = 0.71073Å) radiation. The X-ray generator was operated at 50 kV and 30 mA. A preliminary set of cell constants and an orientation matrix were calculated from three sets of 36 frames. Data were collected with ω scan width of 0.5° at different settings of φ and 2θ with a frame time of 10 sec for **2a**, **3a**, **6b** and 15, 20 sec for **4a**, **5a** respectively, keeping the sample-to-detector distance fixed at 5.00 cm. The X-ray data collection was monitored by APEX2 program (Bruker, 2006). All the data were corrected for Lorentzian, polarization and absorption effects using SAINT and SADABS programs (Bruker, 2006). SHELX-97 was used for structure solution and full matrix least-squares refinement on F^2 . All the hydrogen atoms were placed in geometrically idealized position and constrained to ride on their parent atoms. An ORTEP view of all five compounds were drawn with 50% probability displacement ellipsoids and H atoms are shown as small spheres of arbitrary radii.

Table 7: Crystal data table

	2a	3a	4a	5a	6b
Mol. Formula	C ₂₉ H ₂₅ BN ₂	C ₂₇ H ₂₀ BN	C ₂₉ H ₂₃ BN ₂	C ₂₅ H ₂₀ BN	C ₂₁ H ₂₅ BN ₂
<i>Mr</i>	412.32	369.25	410.30	345.23	316.24

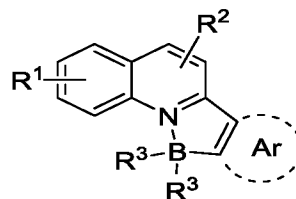
Temp. (K)	200(2)	293(2)	293(2)	150(2)	150(2)
Crystal System	monoclinic	monoclinic	triclinic	monoclinic	triclinic
Space group	$P2_1/n$	$P2_1/c$	$P1$	$P2_1/n$	$P1$
$a/\text{\AA}$	17.3899(3)	8.8980(4)	9.3145(5)	13.9351(7)	7.9636(2)
$b/\text{\AA}$	10.3122(2)	7.0675(3)	9.7778(6)	9.0239(5)	8.8054(2)
$c/\text{\AA}$	26.5129(5)	30.3620(14)	12.5665(7)	14.1194(8)	14.8492(5)
$\alpha/^\circ$	90	90	83.550(3)	90	106.476(2)
$\beta/^\circ$	108.4870(10)	98.000(3)	84.896(3)	92.128(3)	90.570(2)
$\gamma/^\circ$	90	90	76.744(3)	90	116.512(2)
$V/\text{\AA}^3$	4509.15(14)	1890.78(15)	1104.59(11)	1774.28(17)	882.12(4)
$Z, D_{\text{calc}}/\text{g cm}^{-3}$	8, 1.215	4, 1.297	2, 1.234	4, 1.292	2, 1.191
μ/mm^{-1}	0.070	0.074	0.071	0.074	0.069
F (000)	1744	776	432	728	340
$\theta \text{ max}/^\circ$	25.00	25.00	25.00	25.00	25.00
Absor. correction	multi-scan	multi-scan	multi-scan	multi-scan	multi-scan
Refln. collected	63086	13377	15850	22665	12311
Unique refln.	7928	3338	3879	3108	3115
Observed refln.	6507	2420	3046	2911	2747
R_{int}	0.0588	0.0472	0.0305	0.0478	0.0213
No. of Parameter	581	265	291	247	221
$R_{\text{I_obs}}, R_{\text{I_all}}$	0.0776, 0.0965	0.0576, 0.0804	0.0586, 0.0755	0.1623, 0.1655	0.0417, 0.0481
$wR_{\text{2_obs}}, wR_{\text{2_all}}$	0.1548, 0.1640	0.1232, 0.1344	0.1330, 0.1416	0.4284, 0.4295	0.1004, 0.1044
GoF	1.150	1.068	1.114	1.212	1.027
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}/\text{e}\text{\AA}^{-3}$	0.246, -0.255	0.187, -0.198	0.317, -0.200	0.588, -0.596	0.238, -0.188

Advantages of invention:

- Novel N,C-Chelate four-coordinate organoborons of formula (I), wherein said organoborons exhibit tunable solid-state emission colours that cover the whole visible region.
- The compounds exhibit tunable emission both in solution and solid state.
- Compounds are thermally stable, good quantum yields; high stokes shift and show positive solvatochromic behaviour.

WE CLAIM:

1. Novel full-color tunable light emitter based on N,C-chelate four-coordinate organoborons having excellent Quantum yield, stokes shift, fluorescent lifetime and solvate chromism of Formula (I)



(I)

wherein,

R^1 , R^2 and R^3 are selected independently from hydrogen, halogen, (un)substituted alkyl, (un)substituted aryl, (un)substituted heteroaryl, (un)substituted heterocyclic group; said R^1 , R^2 is selected from hydrogen, R^3 is selected from Methyl, Ethyl, n-Octyl, Phenyl;

'ringAr' represent (un)substituted aryl, (un)substituted heteroaryl, (un)substituted heterocyclic group; said Ar is selected from Benzothiophenyl, Pyrenyl, Phenathrenyl, $Ph_2N-C_6H_4$, Carbazole- C_6H_4 , $Me_2N-C_6H_4$;

said Quantum yield is ranging from 0.9 to 0.81;

said stokes shift is in solid state ranging from 93 to 197 and in solution state ranging from 60 to 165;

said fluorescent lifetime is ranging from 2.1 to 6.9;

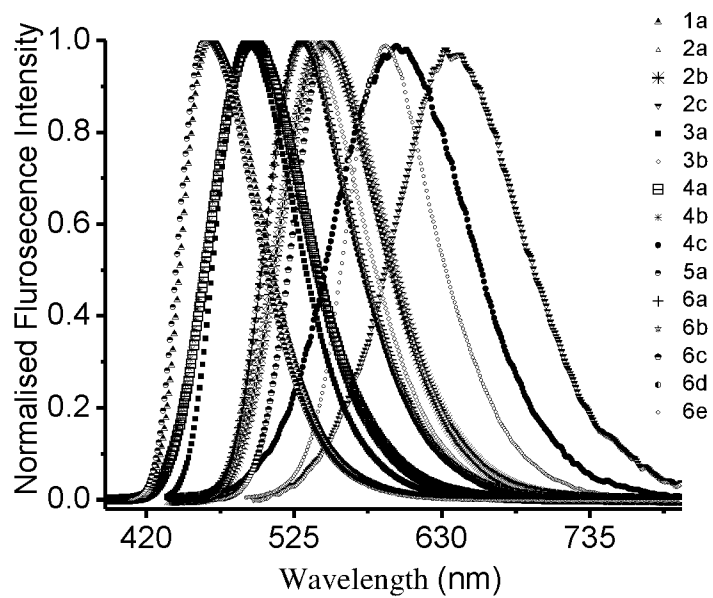
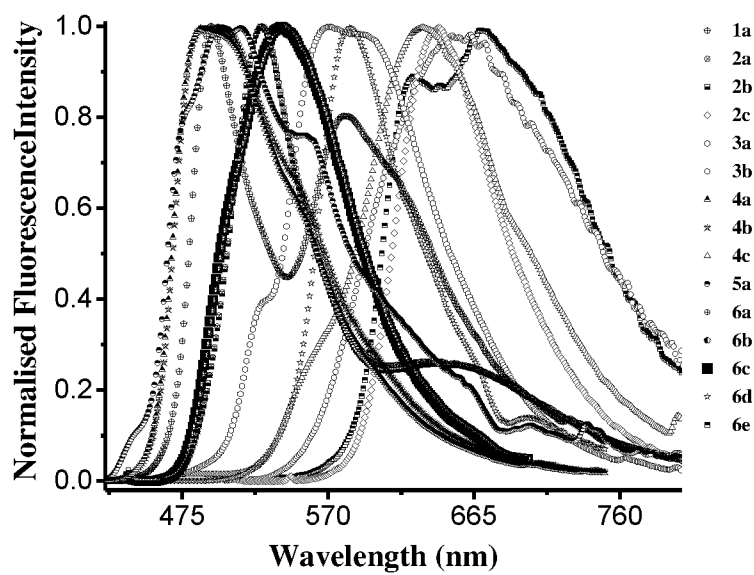
said compound is selected from 12,12-dimethyl-12H-12l4,13l4 benzo[4',5']thieno[3',2':3,4][1,2]azaborolo[1,5-a]quinolone, 11,11-dimethyl-N,N-diphenyl-11H-11l4,12l4-benzo[3,4][1,2]azaborolo[1,5-a]quinolin-9-amine, 11,11-dioctyl-N,N-diphenyl-11H-11l4,12l4-benzo[3,4][1,2]azaborolo[1,5-a]quinolin-9-amine, 11,11-dibromo-N,N-diphenyl-11H-11l4,12l4-benzo[3,4][1,2] azaborolo[1,5-a]quinolin-9-amine, 14,14-dimethyl-14H-13l4,14l4-pyreno

[1',2':3,4][1,2]azaborolo[1,5-a]quinoline, 14,14-dibromo-14H-13l4,14l4-pyreno [1',2':3,4][1,2]azaborolo[1,5-a]quinoline, 9-(9H-carbazol-9-yl)-11,11-dimethyl-11H-11l4,12l4-benzo[3,4][1,2]azaborolo[1,5-a]quinolone, 9-(9H-carbazol-9-yl)-11,11-dioctyl-11H-11l4,12l4-benzo[3,4][1,2]azaborolo[1,5-a]quinoline, 11,11-dibromo-9-(9H-carbazol-9-yl)-11H-11l4,12l4-benzo[3,4][1,2]azaborolo[1,5-a]quinoline, 9,9-dimethyl-9H-9l4,10l4-phenanthro[9',10':3,4][1,2]azaborolo[1,5-a]quinoline,

N,N,11,11-tetramethyl-11H-1114,1214-benzo[3,4][1,2]azaborolo[1,5-a]quinolin-9-amine, 11,11-diethyl-N,N-dimethyl-11H-1114,1214-benzo[3,4][1,2]azaborolo[1,5-a]quinolin-9-amine, N,N-dimethyl-11,11-dioctyl-11H-1114,1214-benzo[3,4][1,2]azaborolo[1,5-a]quinolin-9-amine, N,N-dimethyl-11,11-diphenyl-11H-1114,1214-benzo[3,4][1,2]azaborolo[1,5-a]quinolin-9-amine, 11,11-dibromo-N,N-dimethyl-11H-1114,1214-benzo[3,4][1,2]azaborolo[1,5-a]quinolin-9-amine.

2. The compounds as claimed in claim 1, wherein said compound emits light in solid and solution states.
3. The compounds as claimed in claim 1, wherein the light emission of said compound in visible spectrum is tunable.
4. The compounds as claimed in claim 1, wherein said compound is used in optoelectronic devices.
5. A process for synthesis of N, C-Chelate four-coordinate organoborons of Formula (I) as claimed in claim 1 comprising the steps of:
 - a) reacting 2-amino benzaldehyde with suitable alkyne in presence of metal as catalyst and an amine to obtain 2-substituted quinoline;
 - b) reacting 2-substituted quinoline with BBr_3 in presence of trialkylaluminium (AlR_3) to obtain quinoline-borane complex of Formula (I).
6. The process as claimed in claim 5, wherein said metal catalyst is selected from Au(I) , PPh_3AuCl , AgOTf .
7. The process as claimed in claim 5, wherein said suitable alkyne is selected from 2-ethynylbenzo[b]thiophene, 4-ethynyl-N,N-diphenylaniline, 1-ethynylpyrene, 9-(4-ethynylphenyl)-9H-carbazole, 9-ethynylphenanthrene, 4-ethynyl-N,N-dimethylaniline.
8. The process as claimed in claim 5, wherein said trialkylaluminium is selected from trimethylaluminium, triethylaluminium, trioctylaluminium, triphenylaluminium.

1/2

**Fig: 1a****Fig 1b**

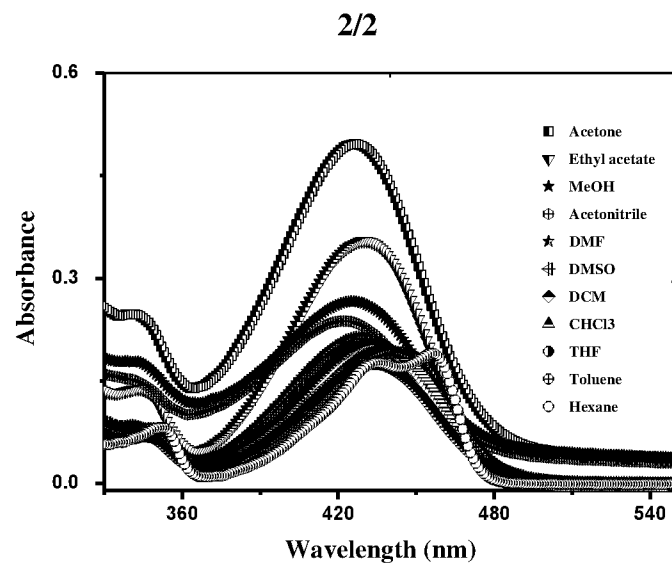


Fig: 2a

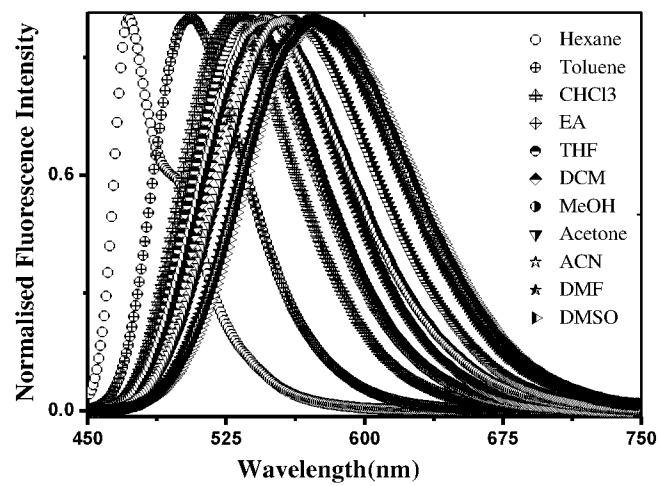


Fig: 2b

INTERNATIONAL SEARCH REPORT

International application No
PCT/IN2016/050193A. CLASSIFICATION OF SUBJECT MATTER
INV. C07F5/02 H01L51/50
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C07F H01L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, CHEM ABS Data, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2011/099331 A1 (UNIV KYOTO [JP]; NIPPON CATALYTIC CHEM IND [JP]; MURAKAMI MASAHIRO [JP] 18 August 2011 (2011-08-18)	1-4
Y	cited in the application claims 1-12; compound 37 ----- -/--	5-8



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

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INTERNATIONAL SEARCH REPORT

International application No

PCT/IN2016/050193

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