Electronic Supplementary Information (ESI)

Functionalized Ruthenium-Graphene Nanosheets Photocatalyst For Highly Regioselective Visible Light Driven C-H Arylation of Imidazo-Pyrimidine

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1. General remarks

RuCl₃, *p*-formyl benzoic acid, 2,4-dimethyl pyrrole, 2,3-Dichloro-5,6-Dicyanobenzoquinone (DDQ), triethyl amine (TEA), boron trifluoride diethyl etherate, N-iodosuccinimide, 4-ethynylbenzaldehyde, Pd(PPh₃)₂Cl₂, CuI and melamine were purchased from Sigma Aldrich. Ultra-pure water was obtained using a Millipore System (Tech Sinhan Science).

2. Instruments and Measurements

Fourier transform infrared spectroscopy (FTIR) spectra were obtained on a Bruker ALPHA-T FT-IR spectrometer. The test specimens were prepared by the KBr-disk method. Wide-angle X-ray diffraction (XRD) analyses were carried out by using an X-ray diffractometer (D/MAX-2200, Rigaku Denki). The X-ray diffraction patterns were recorded in the range of $2\Theta = 5-40^{\circ}$ with Cu K α radiation (λ = 1.5406 Å) at 40 kV and 100 mA. The Brunauer–Emmett–Teller (BET) analysis of the samples were performed on Micromeritics ASAP 2420 system. X-ray photoelectron spectroscopy (XPS) measurements were recorded on Axis Nova photoelectron spectrometer (KRATOS). UV-Vis spectra were acquired using Shimadzu UV-1800 spectrophotometer. The samples for field emission scanning electron microscopy (FESEM) analysis were prepared on Cu mount with Pt coating and examined by Carl Zeiss *\Sigma***IGMA HD** FESEM instrument at 10 kV. High-resolution transmission electron microscope (HRTEM) images were obtained on a FET Phillips instrument [Model No. 200k VLAB6, (FEL TECNAI G2-20S-Twin)] operated at 200 kV. A commercial atomic force microscope (Nanoscope; Digital Instruments, Veeco Metrology group), equipped with a J scanner was used to examine the morphology of the sample in the tapping mode. ¹H NMR spectra were recorded on a Bruker AVANCE II+ 500 MHz spectrometer with tetramethylsilane (TMS; $\delta = 0$) as internal standard.

3. Experimental Section

3.1 Synthesis of RuCl₂(DMSO)₄

 $RuCl_2(DMSO)_4$ complex was prepared as per reported literature.¹ In a 50ml round bottle flask, $RuCl_3$ (0.6g) was mixed in 25 mL of DMSO and refluxed at 190 °C for 20 min. The color of the solution rapidly changed from orange to brown. Upon cooling, acetone was added which led to the precipitation of a yellow crude product. It was recrystallized from hot DMSO, affording yellow crystals of $RuCl_2(DMSO)_4$ compound.

3.2 Synthesis of 4-(5,5-difluoro-1,3,7,9-tetramethyl-5H- $4\lambda^4$, $5\lambda^4$ [1,2-C:2',1'-f][1,3, 2]diazaboriniu-10-yl)benzoic acid (BODIPY)

4-(5,5-difluoro-1,3,7,9-tetramethyl-5H-4 λ^4 ,5 λ^4 [1,2-C:2',1'-f][1,3,2] diazaboriniu-10-yl) benzoic acid (BODIPY) was prepared as per reported procedure.² A 500ml 3-neck round bottom flask was activated with Ar. After 30 minutes, 0.675 g of p-formyl benzoic acid (4.5 mmol), 0.925 g of 2,4-dimethyl pyrrole (9.7 mmol) and 125 ml dichloromethane (DCM) were added. After 15 min, a few drops of trifluoroacetic acid were added, and stirred for 20 hours at ambient temperature. After 20 h, 100 ml DCM containing 1.02 g of DDQ (4.5 mmol) was added, and stirred for further 5 hours at ambient temperature. After this, 2.5 ml of triethyl amine (TEA) and boron trifluoride diethyl etherate (BF₃·O(C₂H₅)₂ were carefully added. After stirring for 12 h the entire solution was treated with water (125 mL) and extracted with DCM. The DCM layer was treated with anhydrous magnesium sulfate (MgSO₄) and concentrated to dryness. Finally, the residue was purified by flash column chromatography using MeOH/DCM (1:30 v/v) as the eluent, affording red colour bodipy dye (1) in 10 % yield. ¹H NMR (500 MHz, MeOD): 8.16 (d, 2H), 7.40 (d, 2H), 6.06 (s, 2H), 2.49 (s, 6H), 1.40 (s, 6H).

3.3 Synthesis of 4-(5,5-difluoro-2-iodo-1,3,7,9-tetramethyl-5H- $4\lambda^4$, $5\lambda^4$ [1,2-C:2',1'-f][1,3, 2]diazaboriniu-10-yl)benzoic acid (iodo-BODIPY)

4-(5,5-difluoro-2-iodo-1,3,7,9-tetramethyl-5H-4 λ^4 ,5 λ^4 [1,2-C:2',1'-f][1,3, 2]diazaboriniu-10yl)benzoic acid (iodo-BODIPY) was prepared as per reported method.³ BODIPY (92 mg, 0.25 mmol), and N-iodosuccinimide (NIS, 56 mg, 0.25 mmol) were mixed in dry DCM (25ml) under Ar, and the reaction mixture was allowed to stir at ambient temperature for 2 h. The completion of the reaction was monitored by TLC. The solvent was then evaporated under reduced pressure and the crude solid product was purified by flash chromatography using MeOH/DCM (1:30 v/v) as the eluent affording the red color solid in 65 % yield (0.16 g). ¹H NMR (500 MHz, DMSO-d₆): d 8.12 (d, J = 8.3 Hz, 2H), 7.55 (d, J = 8.3 Hz, 2H), 6.32 (s, 1H), 2.54 (d, J = 15.8 Hz, 3H), 2.48 (d, J = 16.2 Hz, 3H), 1.33 (d, J = 4.7 Hz, 6H).

3.4Synthesisof4-(5,5-difluoro-1,3,7,9-tetramethyl-2-((4-((oxoλ3-methyl)-
λ3oxidanyl)phenyl)ethynyl)-5H-4λ4,5λ4-dipyrrolo[1,2-C:2',1'-f][1,3,2]diazaboriniu-10-
yl)benzoic acid (ethynyl phenyl-BODIPY)

 $4-(5,5-difluoro-1,3,7,9-tetramethyl-2-((4-((oxo\lambda3-methyl)-\lambda3oxidanyl)phenyl)ethynyl)-5H 4\lambda4,5\lambda4-dipyrrolo[1,2-C:2',1'-f][1,3,2]diazaboriniu-10-yl)benzoic acid (ethynyl phenyl-$ BODIPY) was synthesized by reported procedure.⁴ 4-ethynylbenzaldehyde and mono-iodo- $BODIPY were dissolved in THF along with catalytic amount of TEA. Then Pd(PPh_3)_2Cl_2 (0.03)$ equiv.), PPh₃ (0.03 equiv.), and CuI (0.02 equiv.) were added, and the solution was refluxed for 5 h. The solution was then cooled to ambient temperature, and the solvent was evaporated under reduced pressure. The solid product obtained was dissolved in water and extracted with DCM. The combined organic layer was then dried over anhydrous MgSO₄. The solvent was evaporated under reduced pressure and the crude product was purified by flash column chromatography (silica gel, hexane/DCM = 1:1) to afford ethynyl phenyl-BODIPY as the product (Yield = 25 %).



3.5 Preparation of Nitrogen Doped Graphene Nanosheets (NDGNs)

NDGNs were prepared by a slightly modified literature method.⁵ Graphene and melamine were mixed in a pestle and mortar for 15 min, and the mixture was then transferred in the corundum tube with a flow of 99.9% pure argon (Ar). Ar gas was flowed at the rate of 15 sccm before the furnace was heated to 850°C. Once the furnace attained the targeted temperature, it was maintained at this temperature for 1h. The reaction mixture was then cooled to ambient temperature under Ar atmosphere. Finally, the product was removed from the corundum tube.

3.6 Preparation of Ruthenium-Nitrogen Doped Graphene Nanosheets (RuNDGNs)

In 50ml round bottle flask, **NDGNs** (0.24g) and $RuCl_2(DMSO)_4$ (0.06g) were dissolved in 60 mL of water and refluxed at 100 °C under nitrogen for 3h. Finally, the product was washed with excess ethanol, affording pure **Ru-NDGNs** compound.

3.7 Preparation of BODIPY Functionalized Ruthenium-Nitrogen Doped Graphene Nanosheets *via* 1,3-dipolar cycloaddition method (fRuNDGNs)

Ru-NDGNs were functionalized by reported method.^{6,7} Ru-NDGNs (50mg), BODIPY (3eq. w/w) and N-methyl glycine (3eq.w/w) were dissolved in 25 ml ortho-dichlorobenzene (ODCB) in the presence of catalytic amount of TEA and heated at 80 °C for 96 h. The resultant mixture was filtered through membrane filter (0.45 μ m filter), and the solid product was washed thoroughly with methanol until the solvent was clear. Finally, product was dispersed in 20 mL DMF and sonicated. After sonication, the solvent was decanted and the fRuNDGNs was washed with a small amount of water to remove leftover impurities. It was eventually dried under vacuum to yield the hybrid fRuNDGNs photocatalyst.

3.8 Visible light driven C-H arylation

The visible light driven C-H arylation of imidazo[1,2- α]pyrimidines was performed within a quartz reactor at room temperature, using a 450W Xenon lamp (Newport 66921) with a 420 nm cut-off-filter as light source. The isolation and purification of the products were carried out by conventional aqueous workup. The reaction mixture was poured in water followed by extraction of the product in chloroform. The organic layer was dried over magnesium sulphate and concentrated to dryness under reduced pressure. The yield and selectivity of product formed was calculated from ¹H NMR data.

Optimization studies: The reaction mixture consisted of 0.5 mg of photocatalyst (fRuNDGNs/ RuNDGNs/ BODIPY/ BODIPY1/ CCG-BODIPY), Imidazopyrimidine (5 mmol), bromobenzene (5 mmol) and base (Et₃N/ iPr₂EtN) in 3.1 ml of various solvents (MeCN/DMSO/DMF). The mixture was irradiated under visible light with constant stirring for the specified time durations and then analyzed as described above.

Substrate scope studies: The reaction mixture consisted of **fRuNDGNs** (0.5 mg), Imidazopyrimidine (5 mmol), aryl bromo derivative (5 mmol) and Et₃N (10 mmol, 2 eq.) in 3.1 ml of MeCN. The mixture was irradiated under visible light with constant stirring for 12 h and then analyzed as described above.

Catalytic efficiency: The efficiency of the **fRuNDGNs** photocatalyst ranges between 1930 to 2640 $g_{product}$ per $g_{photocatalyst}$ depending on the products as shown in the table S1 below.

S.No.	Product	Catalytic efficiency		
		$(g_{product}/g_{photocatalyst})$		
1.		1930		
2.		2100		
	F			
3.		2350		
4.		2320		
5.		1940		

Table S1. Efficiency of the photocatalyst with various products obtained.

6.		2180
7.	CHO	2200
8.		2640
9.	CCH₃	2230
10.	N N N(CH ₃) ₂	2350

4. Characterization data

4.1 FTIR studies

The Fourier transform infrared (FTIR) spectrum showed (Fig. S3) that the NDGNs produced in the hydrothermal synthesis included a few oxygenated functional groups, and there was no big difference after incorporation with ruthenium ions (RuNDGNs). The broad peak at 3232 cm⁻¹ was attributed to O-H stretching vibrations while the bands at 3035 and 2914 cm⁻¹ may be attributed to the sp² and sp³ C-H stretching, respectively. Similarly the band at 1689 cm⁻¹ may be attributed to C=O, whereas the bands between 1622 and 1278 cm⁻¹ likely arise from C=C while the band at 1166 cm⁻¹ may be attributed to from C–O and C–N. The FT-IR spectrum of fRuNDGNs exhibited C-H stretching at 2929 and 2856 cm⁻¹ that are absent in the FTIR spectrum of RuNDGNs. Besides C-O stretching at 1270 cm⁻¹, O–H stretching at 3425 cm⁻¹, CH₂- stretch band at 2856 cm⁻¹, and -C=C- stretch multiple bands between 1657 and 1495 cm⁻¹, the B-N stretching band at 1085 cm⁻¹ attributed to the presence of B-N group provided evidence for successful functionalization of BODIPY.^{8,9}

4.2 Raman studies

Raman spectra of NDGNs showed two vibrational bands at 1332 and 1562 cm⁻¹, characteristic of the D (disorder) and G (graphitic) bands of graphene derivatives (Fig. S4).¹⁰⁻¹³ After incorporation of ruthenium ions, D and G bands of NDGNs shifted to 1368 and 1594 cm⁻¹ and the intensity ratio (I_D/I_G) of the D and G band was found to increase from 0.91 (NDGNs) to 0.95 (RuNDGNs), consistent with the incorporation of ruthenium ions with pyridinic N atoms in NDGNs that resulted in structural distortion of the graphene sheets.⁶ On the other hand, D and G bands in fRuNDGNs appeared at 1373 and 1612 cm⁻¹, respectively. The shift in peak

position of D (5 cm⁻¹) and G (18 cm⁻¹) bands can be clearly attributed to the covalent attachment of BODIPY to RuNDGNs.^{14,15} In addition, fRuNDGNs also show increased intensity ratio (I_D/I_G) of the D and G band from 0.95 (RuNDGNs) to 1.12 (fRuNDGNs). The increased I_D/I_G ratio is consistent with the functionalization of RuNDGNs through covalent bonding.^{6,14,15}

4.3 TGA analysis

The loading of BODIPY in the fRuNDGNs hybrid molecule was determined by thermogravimetric analysis (TGA). Figure S5 shows the TGA curves of NDGNs, RuNDGNs, and fRuNDGNs. The fRuNDGNs photocatalyst show two major weight losses near about 23 % and 14 %, relative to NDGNs and RuNDGNs, between 350 and 800 °C. This weight loss corresponds to the loss of BODIPY molecules covalently attached to RuNDGNs via 1,3-dipolar cycloaddition. Accordingly, the degree of functionalization was calculated to be one BODIPY molecule per 139 carbon atoms in fRuNDGNs.⁶

4.4 XPS studies

To probe the effect of ruthenium doping, X-ray photoelectron spectroscopy (XPS) measurements were made to investigate NDGNs based samples, and also inveterate the attachment of the BODIPY to the RuNDGNs via 1,3-dipolar cycloaddition.¹⁶ From the C1s deconvolution spectra, five peaks were observed (Fig. S6). The peak observed at 281.8 can be assigned to the Ru electrons of Ru(II)-pyridine moieties along with C=C, C-N/C-C, C-O and O-C=O at 284.6, 286.1, 287.2 and 289 eV, respectively.¹⁷⁻²⁰ Again, this indicated that the ruthenium ions were incorporated into the skeleton of NDGNs. Similarly, three peaks can be recognized in deconvolution of the N1s spectrum in Figure 3b at 396.0, 397.1 and 399.4 eV, which may be attributed to the pyridinic, pyrrolic and graphitic N, respectively.²¹⁻²³

Interestingly, in comparison with the NDGNs,¹⁷ whereas the binding energies of the graphitic and pyrrolic nitrogen remained virtually unchanged, the pyridinic nitrogen showed a shift near about 0.4eV in RuNDGNs. It should be noted that this shift in N1s binding energy has been observed upon the formation of Ru (II)-pyridine complexes.²⁴ This suggests that incorporation of the ruthenium ions into the NDGNs most probably by the complexation between pyridinic nitrogen and Ru(II),²⁵ leading to apparent division of the nitrogen electrons, as complexation interactions with other nitrogens were negligible. Furthermore, after functionalization with BODIPY, the spectra of fRuNDGNs show a new peak that is ascribed to C1s, and N1s, confirming the formation of BODIPY grafted RuNDGNs.^{6,26,27} In contrast to RuNDGNs, the binding energies of the N1s of fRuNDGNs are 396.45, 397.5 and 398.6 eV, and there is a considerable intensity of the N1s peak increase because of numerous chemical environments.

4.5 Powder XRD studies

The PXRD pattern (Fig S7) of NDGNs showed a peak around 26.5° with an interlayer space of ~0.34 nm which is similar to that reported earlier for N-doped graphene.⁵ This result also demonstrated that the graphitic crystal structure was largely preserved following nitrogen doping. A similar peak was also observed in case of RuNDGNs and fRuNDGNs which indicated that the NDGNs backbone was largely preserved after Ru(II) and BODIPY attachment. However an additional peak was observed at 28.5° which can be attributed to the

change in graphene backbone following covalent attachment of BODIPY by Diels Alder reaction.

4.6 BET surface area analysis studies

The fRuNDGNs exhibited type IV isotherm that indicated well-defined mesopores (Fig S8). Moreover the H3-type hysteresis loop in fRuNDGNs was indicative of the presence of slit-like pores. Besides this, a slightly broad pore-size distribution in the 40 nm region was observed. The BET surface area of fRuNDGNs was found to be 12.1 m² g⁻¹ which is higher than that observed for N-doped graphene (~6 m² g⁻¹) in literature⁶ and can be attributed to attachment of Ru(II) and BODIPY on NDGNs.



Fig. S1 AFM (3D and roughness images), SEM, and TEM images of (a) NDGNs, (b) RuNDGNs, and (c) fRuNDGNs.



Fig. S2 UV-Visible absorption spectrum of BODIPY, RuNDGNs, and fRuNDGNs.



Fig. S3 FTIR spectra of NDGNs, RuNDGNs, and fRuNDGNs.



Fig. S4 Raman spectra of the NDGNs, RuNDGNs, and fRuNDGNs.



Fig. S5 TGA of the NDGNs, RuNDGNs, and fRuNDGNs.



Fig. S6 (a, b) C1s and N1s X-ray photoelectron (XPS) spectra of RuNDGNs, and (c, d) C1s and N1s X-ray photoelectron spectra of fRuNDGNs.



Fig. S7 Powder XRD pattern of NDGNs, RuNDGNs and fRuNDGNs.



Fig. S8 Nitrogen adsorption-desorption isotherms of fRuNDGNs photocatalyst with the corresponding pore size shown in inset.

6. ESR mechanism

As shown in Figure S9 the ESR spectra of RuNDGNs displayed first derivative signal with a near symmetric partition of the amplitude. The ESR signal of BODIPY contributed by the conducting electrons appeared at g value of 1.9932 (in which g is the electron factor) with δ H_{pp} of 5G (δ H_{pp} is the peak-to-peak separation),²⁸ whereas RuNDGNs exhibit a relatively narrow ESR signal with a higher g value of 1.9987 and δ H_{pp} of 3G, which indicated an electron-transfer trend from the RuNDGNs to the BODIPY.



Fig. S9 ESR spectra along with 3D structures of (a) RuNDGNs and (b) BODIPY.

Table S2 Literature examples on Pd(II) catalyzed C-H arylation of Imidazo[1,2-*a*]pyrimidine with bromobenzene

S.No.	Catalyst/Ligand	Base	Solvent	Temperature	Yield	Reference
				(°C)	(%)	
1.	$Pd(OAc)_2/Ph_3P$	Cs ₂ CO ₃	Dioxane	100	97	W. Li, D. P. Nelson,
						M. S. Jensen, R. S.
						Hoerrner, G. J. Javadi,
						D. Cai, and R. D.
						Larsen, Org. Lett.,
						2003, 5 , 4835
2.	$Pd(OAc)_2/Ph_3P$	Cs ₂ CO ₃	Dioxane	145 (with	96	D. S. Ermolat'ev, V. N.
				microwave		Giménez, E. V.
				irradiation)		Babaev, and E. Van der
						Eycken, J. Comb.
						Chem., 2006, 8, 659

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