Dalton Transactions

PAPER

View Article Online
View Journal | View Issue

Cite this: *Dalton Trans.*, 2018, **47**, 8466

Coordination-driven self-assembly of ruthenium(II) architectures: synthesis, characterization and cytotoxicity studies†

Aderonke Ajibola Adeyemo,[a] Abhijith Shettar,[b,c] Imtiyaz Ahmad Bhat,[a] Paturu Kondaiah*[b] and Partha Sarathi Mukherjee *[a]

Received 13th March 2018,
Accepted 31st May 2018

DOI: 10.1039/c8dt00962g

rsc.li/dalton

Coordination-driven self-assembly of organometallic η^6-arene ruthenium(II) supramolecular architectures (**MA_1–MA_4**) was carried out by employing dinuclear ruthenium acceptors $[Ru_2(\mu\text{-}\eta^4\text{-}C_2O_4)(CH_3OH)_2(\eta^6\text{-}p\text{-cymene})_2](CF_3SO_3)_2$ (**Ru_a**), $[Ru_2(\mu\text{-}\eta^4\text{-}C_6H_2O_4)(CH_3OH)_2(\eta^6\text{-}p\text{-cymene})_2](CF_3SO_3)_2$ (**Ru_b**), $[Ru_2(dhnq)(H_2O)_2(\eta^6\text{-}p\text{-cymene})_2](CF_3SO_3)_2$ (**Ru_c**) and $[Ru_2(dhtq)(H_2O)_2(\eta^6\text{-}p\text{-cymene})_2](CF_3SO_3)_2$ (**Ru_d**) separately with a new tetratopic donor (**TD**) in methanol at room temperature [**TD** = *N*,*N*,*N*′,*N*′-tetra(pyridin-4-yl)-[1,1′-biphenyl]-4,4′-diamine]. All the coordination architectures were characterized by using spectroscopic techniques. The potency of these self-assembled architectures against human cervical cancer HeLa and human lung adenocarcinoma A549 cell lines is explored *in vitro* using MTT (3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide), annexin V-FITC/PI and 2′,7′-dichlorofluorescein-diacetate assays.

Introduction

Self-assembly is a process that provides a simple and systematic arrangement of two or more components (molecules) into supramolecular structures with specific dimensions.[1–5] It is a thermodynamically driven and dynamic technique wherein the most stable architecture is obtained in moderate to high yield.[2,6,7] Moreover, a high degree of symmetry is often found in the final architecture[8] which is extremely difficult to prepare by conventional or stepwise covalent synthetic methods.[9] An exceptional approach to obtain organometallic supramolecular architectures with well-defined shapes and cavity is coordination-driven self-assembly with a distinct advantage of a single-step reaction process requiring metal ions and predesigned ligands under mild reaction conditions.[10–19] The coordination-driven self-assembly utilizing transition metals to build self-assembled supramolecular architectures has some advantages which include (i) diverse bonding modes and geometrical symmetries of d-orbitals as compared to simple organic molecules, (ii) a wide range of sizes (lengths), shapes, and electronic and steric properties that can be fine-tuned in the bridging ligands and (iii) spectral, magnetic, redox, photophysical and photochemical properties that can be embedded to provide superior features to the final discrete 2D and 3D supramolecular architectures by the rational selection of complementary building blocks with fascinating geometries and functional groups (rigid and/or flexible electron-poor metal centres and rigid and/or flexible electron-rich organic donors).[20–28]

Interestingly, the discovery of cisplatin and its derivatives in the 1960s laid the first stone for the subsequent development of metal-based anti-tumour agents.[29–34] Various transition metal complexes other than platinum complexes with different oxidation states and ligands of diverse structures have been reported for their anti-tumour properties leading to a range of coordination geometries which provide transition metal complexes with unique functionalities compared to pure organic molecules.[35–40] The electrostatic attraction between the positive charge of transition metals and the negative charge of many biological structures such as nucleic acids (DNA and RNA), some phospholipids and some regions on the protein molecules facilitates their binding with intracellular targets.[41–46] However, the transfer of interest away from platinum towards ruthenium for the development of novel anti-

[a]*Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore-560012, India. E-mail: psm@iisc.ac.in; Fax: +91-80-23601552; Tel: +91-80-22933352*
[b]*Department of Molecular Reproduction, Development and Genetics, Indian Institute of Science, Bangalore-560012, India. E-mail: paturu@iisc.ac.in; Fax: +91-80-23600999; Tel: +91-80-22932688*
[c]*Department of Biotechnology Engineering, Ramaiah Institute of Technology, Bangalore-560064, India*

† Electronic supplementary information (ESI) available: Infra-red spectra, ^1H, ^{19}F, ^{13}C, ^1H–^1H COSY, DOSY NMR spectra, ESI-MS data and cell viability plots of the molecular architectures. CCDC 1815599. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c8dt00962g