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Editor's Page

Shining Light on Organometallic Chemistry

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Solar energy conversion drives life on Earth. Artificial photochemistry, on the other hand, has traditionally targeted inorganic semiconductors, organic transformations as exemplified by thermally forbidden [2 + 2] cycloadditions and the activation of diazo- and azide functional groups, metal-organic coordination compounds such as $[Ru(bipy)_3]^{2+}$ and the Creutz−Taube ion, and theory-/spectroscopy-driven approaches. Hence, organometallic photochemistry has long been limited to essentially simple metal−ligand bond cleavage reactions.[1] Interdisciplinary by nature, organometallic photochemistry matured over the last 20 years to represent now its own field of research. This development was driven mainly by two advancements: These are (i) research on strongly bonded C-donor ligands, which allowed for the synthesis of stable complexes with large ligand-field splitting and long-lived excited states, thus rendering them suitable chromophores/luminophores for photocatalysis, photovoltaics, and organic light-emitting devices (OLEDs), and (ii) the enhanced understanding of open-shell reaction mechanisms, which paved the way for photoredox catalysis, enabling previously unfeasible "dream reactions". In fact, abundant photoredox-catalytic protocols nowadays rely on organometallic sensitizers. Particularly successful photocatalysts are tris(2-phenylpyridine)iridium and its derivatives. This 3-fold cyclometalated complex had been first synthesized in high yield by Watts and colleagues in 1991.[2] The strong spin−orbit coupling induced by the heavy element iridium largely eliminates the spin-forbidden nature of the phosphorescent transitions in this complex, thus rendering it suitable for a vast range of applications requiring high quantum yields of excited states with long lifetime at room temperature. Although this complex did not receive vast attention until subsequent work by the Thompson group in 2001,[3] it is now one of the main workhorses in the field, as demonstrated by the contribution by Dang and Teets featured herein (10.1021/acs.organomet.3c00491). Despite their superior photophysical properties, the major current challenge in this field is the desire to replace heavy and noble metals such as iridium, platinum, and gold with earth-abundant 3d or main-group metals.[4] While there is still a long way to go, modern organometallic chemistry is developing solutions, as exemplified by Heinze and colleagues' contribution to this special issue, which reports on spin-flip emissive cyclometalated chromium(III) complexes (10.1021/acs.organomet.4c00075). A complementary approach is presented by the Haas group, who reports how the irradiation of acyl silanes induces Brook-type rearrangement reactions (10.1021/acs.organomet.3c00531).

This special issue "Shining Light on Organometallic Chemistry: Synthesis, Mechanisms, and Applications Driven by Photochemistry" celebrates current photochemistry with molecular organometallic compounds. The feature articles mentioned above represent the two directions of the special issue: six contributions address (i) the design and characterization as well as application of luminescent organometallics, and four contributions target (ii) photo-organometallic approaches to the synthesis of fine chemicals.

Stipurin and Strassner studied cyclometalated *N*-heterocyclic C^C* platinum complexes, supported by bis(pyridyl)- and bis(pyrazolyl)borate ligands (10.1021/acs.organomet.3c00532). Demonstrating the versatility of the field, this contribution comprises air-sensitive organometallic synthesis and structural characterization in the solid state, spectroscopy (UV−vis absorption/emission in solution and solid state, cyclic and differential pulse voltammetry, time-resolved single photon counting TCSPC) and quantum chemical calculations. The authors find that the emissive properties are controlled by the organometallic C^C* moiety, whereas the ancillary *N*-donor-borate ligands tune only the emission quantum yields (10−90%). Corresponding characterization techniques also find use in Stein, Förster, and Heinze's contribution on tris-cyclometalated P^C and N^C chromium(III) spin-flip emitters (10.1021/acs.organomet.4c00075). These emitters do not harness common charge-transfer transitions, yet promote metal-centered $^4A_2 \leftarrow {}^2E/{}^2T_1$ spin-flip emission in pseudo-octahedral coordination. Key to this design concept are the strong-field phenyl ligands, which prevent excited state deactivation via back-intersystem crossing. In fact, the pendant amine and phosphine ligands are labile in solution, thus hampering their usefulness in optical applications of such chromium(III) complexes. Romanov, Linnolahti, and colleagues present an investigation on diamido-carbene (DAC)-supported gold(I) emitters (10.1021/acs.organomet.3c00360). Peculiar ring-opening of the carbene was observed in the presence of KO^{t}Bu, thereby affording an intriguing Au_3 triangle, whereby each gold ion is coordinated by an acyclic, N,O-substituted carbene. The corresponding (DAC)AuX precursor molecules were found to not exhibit a ligand-centered, dark triplet ^{3}LC state as the lowest in energy triplet state. This prompted the authors to move away from conventional NHC use for gold(I) emitters and to foresee a

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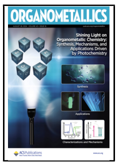

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brighter future for strong acceptor carbenes just as the DAC itself. Strassert et al. present two detailed investigations on $^1O_2$ photosensitization by CNN and NNN pincer-type ligand supported platinum(II), palladium(II) and related rhenium(I) complexes (10.1021/acs.organomet.3c00539; 10.1021/acs.organomet.3c00540). The switch from platinum to palladium results in weaker ligand field splitting and reduced spin−orbit coupling, thereby boosting excited-state lifetimes without luminescence at room temperature, and enabling dual-emission in the case of thiophenyl decoration. *In vitro* (photo)-cytotoxicity studies conducted on human telomerase reverse transcriptase-immortalized cells demonstrated their potential for photodynamic therapy. The contribution by the Haas group (10.1021/acs.organomet.3c00531) presents a study on mono- and bis(acyl)polysilanes and their photoinduced Brook-type rearrangement via transient silenes, thus complementing the other contributions targeting d-block complexes from a p-block perspective.

Dongbang reviewed the latest advancements in metalla-photoredox-catalyzed C(sp^3)−C(sp^3) cross-coupling, which has opened important new molecular space (10.1021/acs.organomet.3c00537). Specific emphasis is put on the mode of activation of the C(sp^3) precursors, namely via metal-based reduction, oxidation by the photocatalyst, hydrogen or halogen atom transfer, or photosensitization leading to subsequent homolytic bond cleavage. The specific modes of activation are then used to systematically categorize the literature precedents, hence presenting the field in a concise and detailed manner. Exploring a related theme of photocatalyzed cross-coupling, Xue et al. discuss a nickel-based photocatalyst that enables the sulfamidation of aryl chlorides with soluble and mild organic amines as bases (10.1021/acs.organomet.3c00506). This photochemical C−N coupling reaction proceeds selectively even in the presence of multiple NH_2 groups and presents unprecedented substrate scope with electron-rich (hetero)aryl chlorides, including the direct synthesis of sulfonamide drug molecules. The photohydrogenation of ketones, aldehydes, and imines under blue light is described by Dang and Teets (10.1021/acs.organomet.3c00491). Using the strong excited-state reducing power of cyclometalated Ir(2-phenylpyridine)$_2$(nacnac) in combination with the sacrificial hydrogen donor BIH (1,3-dimethyl-2,3-dihydro-2-phenylbenzimidazole) prevents the undesired homocoupling to diols and diamines and switches the selectivity instead to C═N/C═O hydrogenation with reduction potentials as negative as −2.57 V versus the Fc/Fc^+ redox couple. Meng, Ji, and Jiang describe a metal-oxo uranyl photocatalyst that harnesses a ligand-to-metal charge transfer (LMCT) excitation with high oxidation potential ($E°$ = +2.6 V vs SHE) to achieve the deprotection of benzyl groups under oxidative conditions (10.1021/acs.organomet.4c00080). The catalytic procedure is straightforward, scales well, is compatible with moisture and air, tolerates nitro, cyano, phenol, and carbonyl functional groups, and hence presents a convenient route to pharmaceuticals and organic materials.

This special issue shines light on photoactive organometallic complexes and their applications as photoredox catalysts. We think that this collection provides an overview on the current achievements and limitations in the field and hope that it sparks the excitement of junior researchers to discovering future breakthroughs for cost-effective and sustainable solar energy conversion. The future is shining bright for organometallics!

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Biographies

Debashis Adhikari is currently an associate professor of Chemistry in IISER Mohali, India. He earned his Ph.D. in inorganic chemistry from Indiana University, Bloomington, and performed postdoctoral research in Northwestern University, Evanston. His group focuses on redox-active ligands applied towards homogeneous catalysis, borrowing hydrogen reactions, and making strong photo-oxidants and reductants under visible light.

Sun Dongbang (Ph.D. 2020) is an assistant professor in the Department of Chemistry at Sogang University, South Korea. Her Ph.D. and postdoctoral studies have centered around total synthesis of natural products and methodology development using transition metals to construct structurally complex motifs. The current group's research interests lie in the development of new transition-metal catalysis using earth-abundant metals and photoredox-catalyzed synthetic methods.

Xuefeng Jiang (Ph.D. 2008) is a Professor for Organic Chemistry at East China Normal University, China. He earned his Ph.D. in Organic Chemistry from the Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, and conducted postdoctoral research at the Scripps Research Institute in the United States. Currently, his research group focuses on: total synthesis of medicinal natural products and functional materials driven by synthetic methodology innovation; high-end instrument development, synthesis automation, and intelligence guided by scientific nature modeling; with a particular focus on photo/electrocatalytic activation of chemical bonds and their industrial applications.

Dominik Munz (Ph.D. 2013) is Professor for Coordination Chemistry at Saarland University, Germany. Research in the group targets zwitterionic organometallics and diradicals with a specific interest for bond activation chemistry, catalysis, mechanisms, spectroscopic properties and—of course—their photophysics.

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