Synthesis and Photophysical Properties of Laterally Asymmetric Digold(I) Alkynyls and Triazolyl: Ancillary Ligand and Organic Functionality Dictate Excited-State Dynamics

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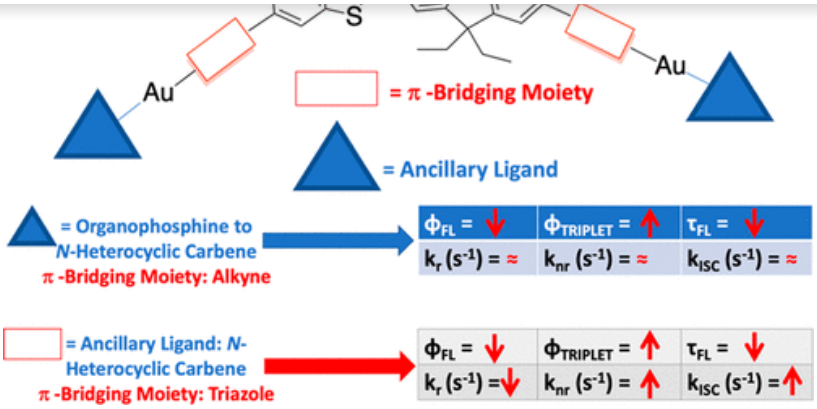

Four new laterally asymmetric dinuclear gold(I) complexes made from a new chromophoric ligand (**Au-DiBTF0–3**) have been characterized. Changing the organic ancillary ligand from a phosphine ((**Au-DiBTF0** (PMe_3) and **Au-DiBTF1** (PCy_3)) to an N-heterocyclic carbene (**Au-DiBTF2**) with an alkynyl linking moiety or modifying the alkynyl linkage to a triazolyl moiety with the ancillary ligand being an N-heterocyclic carbene (**Au-DiBTF3**) impacts the ground- and excited-state properties of these systems. All four complexes exhibit structured absorption and emission spectra with weak phosphorescence. A bathochromic shift is observed in both the ground-state absorption and luminescence spectra as the series varies from **Au-DiBTF0** to **Au-DiBTF3**. The dinuclear alkynyl complexes (**Au-DiBTF0–2**) display decreased fluorescence lifetimes and fluorescence quantum yields along with more efficient intersystem crossing when the capping ligand is changed from a trialkylphosphine to an N-heterocyclic carbene. This change results in comparable rates of radiative decay and intersystem crossing and negligible rates of nonradiative decay. Changing the π-bridging moiety (**Au-DiBTF3**) results in a diminished fluorescence quantum yield, shorter fluorescence lifetime, and increased intersystem quantum yield, resulting in faster intersystem crossing accompanied by slower radiative decay and more efficient nonradiative decay relative to the alkynyl-bridged complexes. Density functional theory calculations are in accord with the observed photophysics, with nearly identical S_1-to-T_2 energy gaps for the dinuclear alkynyl complexes (**Au-DiBTF0** and **-2**) and a smaller energy gap for **Au-DiBTF3**. Experimentally, **Au-DiBTF3** has the highest rate constant and quantum yield of intersystem crossing of the new gold(I) organometallics.

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.9b00768.

- Experimental details, synthetic procedures, and computational and crystallographic data (PDF)
- Cartesian coordinates (XYZ)

Accession Codes

CCDC 1953525 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax: +44 1223 336033.

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