

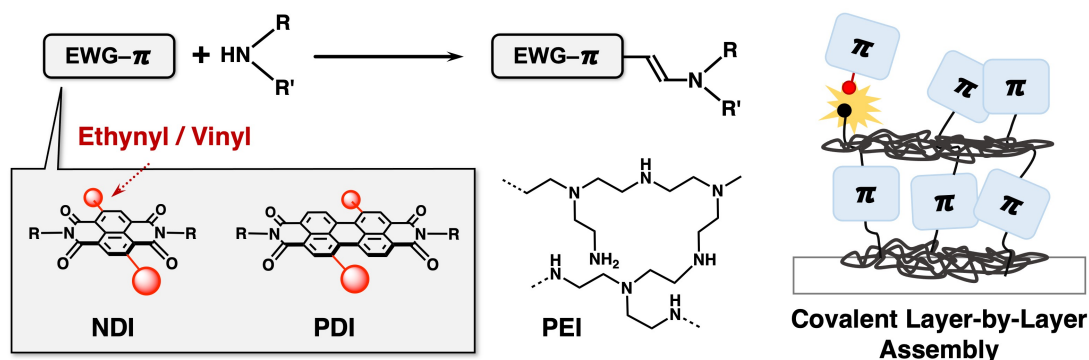
Surface Modification of Polyethylenimine Films with π -Conjugated Molecules via a Catalyst-Free Click Reaction

(¹National Institute for Materials Science, ²University of Tsukuba) ○Lara Rae Holstein,^{1,2} Masayuki Takeuchi,^{1,2} Atsuro Takai¹

Keywords: Click Chemistry; Naphthalenediimide; Organic Thin Films; Polyethylenimine

Polyethylenimine (PEI) films are promising coating materials in organic devices due to their electron rich nature and wide availability in the market.¹ Modification of such polymer coatings with organic functional molecules is expected to provide novel functionality and interfacial control. Previously, we found that ethynyl and vinyl groups appended to electron-accepting π -conjugated systems, such as naphthalenediimides (NDIs) and perylenediimides (PDIs), efficiently react with amines under mild conditions without need of a catalyst.² We envision that this unusual reaction will provide us with a novel, facile approach to free modulation of surface properties of PEI films by forming covalent bonds between the amines of PEI and the π -core of electron acceptors, which is distinct from conventional non- π -conjugated layer-by-layer assembly of PEI films.³ Herein, we report various π -functionalized films by exposing PEI coated surfaces to ethynyl-substituted NDI or PDI solutions in a layered manner.

Silicon, ITO, and quartz substrates were thoroughly cleaned and immersed in a PEI solution, then rinsed and dried under N₂. Next, the substrates were immersed in an ethynyl- or vinyl-substituted NDI solution before being rinsed and dried under N₂. This cycle was repeated n times to obtain (PEI/NDI) _{n} multilayer films. The layer-by-layer buildup was monitored by water contact angle measurements, FT-IR, AFM, UV-vis absorption spectroscopy, and cyclic voltammetry. We will also systematically present how the optical and electronic properties of these films are modulated by simple changes in molecular design.



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