Novel Ladder-type Oligo($\rho$-phenylene)s for Highly Efficient
Multiphoton Absorption and Fused Aromatic-Based Copolymers
for Optoelectronic Applications

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Abstract

To probe the structure-multiphoton property relationship and develop efficient multiphoton absorbers for potential applications, several novel series of well-defined two-dimensional (2D) and three-dimensional (3D) ladder-type oligophenylenes, including linear and symmetrically endcapped diphenylamine derivatives, namely \((L)-\text{Ph}(n)-\text{NPh}\) \((n = 3-8)\); linear and non-endcapped derivatives, namely \((L)-\text{Ph}(n)\) \((n = 3-5)\); star-shaped ladder-type derivatives, namely \(\text{N}(\text{TL})-\text{Ph}(3)-\text{NPh}\), \(\text{N}(\text{TL})-\text{Ph}(3)-\text{CBZ}\), \(\text{TA}(\text{TL})-\text{Ph}(3)-\text{NPh}\) and \(\text{N}(\text{TL})-\text{Ph}(3)-\text{TAZ}\), have been designed and synthesized. In addition, new fused aromatic-based D-A copolymers derived from 5,6-dialkynaphthodithiophene (NDT) and thieno[3,4-c]pyrrole-4,6-dione (TPD), namely PNDTTPD, PNDTTPDT-1, PNDTTPDT-2 and PNDTTPDT-3, have been designed and synthesized via a convergent route. All the newly synthesized molecules were fully characterized with \(^1\text{H}\) NMR, \(^{13}\text{C}\) NMR, HRMS, elemental analysis or GPC and found to be in good agreement with the desired structures.

The chemical and physical properties of these newly synthesized 2D and 3D ladder-type oligophenylenes were investigated including linear optical properties such as UV-vis absorption, emission and fluorescence quantum yield in different solvent; nonlinear optical properties involving power dependent fluorescence intensity and multiphoton absorption (MPA) cross-section, MPA induced lasing characteristics as well as thermal stability. It was demonstrated that novel linear
D-π-D quadrupolar molecules showed great potential for various practical MPA applications. Furthermore, the optical and electrochemical properties of novel fused aromatic–based D-A PNDTPPD and PNDTPPDTs copolymers were investigated by UV-vis absorption in both solution and thin-film, cyclic voltammetry, gel permeation chromatography and thermal stability. A preliminary result of organic field-effect transistor (OFET) study showed that these copolymers would be able to utilize for applications of OFETs and organic photovoltaic cells (OPVs).

The molecular structures of the newly developed molecules, oligomers and polymers are showed as follows:
(L)-Ph(3)  

(L)-Ph(4)  

(L)-Ph(5)  

(L)-Ph(4)-NPh  

(L)-Ph(5)-NPh  

(L)-Ph(3)-NPh  

(L)-Ph(6)-NPh
N(TL)-Ph(3)-CBZ
R = C_{10}H_{21}

N(TL)-Ph(3)-TAZ
R = C_{10}H_{21}
TA(TL)-Ph(3)-NPh

R = C_{16}H_{21}
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