Molecular Barrier-Assisted Multi-Step FRET Enabling Full-Color-Emissive Cocrystals based on ACQ chromophores

Qian Zhou, †[1,2] Shuai Xue,†[1] Xiaomin Zhang,[1] Lijian Ning,[1] Yuhui Song,[1] Yanli Wang,[1] Jinkun Feng,[1] Qiuyu Gong,*[3] Yinjuan Huang.*[1]

[1] State Key Laboratory of Porous Metal Materials, Shanxi International Research Center for Soft Matter, School of Materials Science and Engineering, Xi'an Jiaotong University, Xi'an 710049, P. R. China

[2] Clean Energy Business Department, Shaanxi Transportation Holding Green Development Group Co., Ltd.

* Corresponding Author(s): huangyj@xjtu.edu.cn; gongqiuyu@xjtu.edu.cn

† Equally contributed.

1. Materials

All the materials were provided by Sigma-Aldrich company and used directly unless otherwise specified. Octafluoronaphthalene (OFN, 96%), bis(phenylethynyl)anthracene (BPA, 98%) and bis(phenylethynyl)naphthacene (BPN, 98%), were provided by Sigma-Aldrich. Phenanthrene (Phe，97%) w purchased from Beijing Kaiguo Technology Co., Ltd. Polyvinyl alcohol (PVA, Mw = 31000 ~ 50000) was purchased from Aladdin. Tetrahydrofuran (THF, 99%) was purchased from Merck. Methanol (MeOH, 99%) is supplied by Xi'an kaino Chemical Co., LTD. Copper specimen grids with ultrathin carbon support film (thickness ≤ 3nm, ZB-C4000) were provided by Beijing Zhongxing Bairui Technology Co., Ltd. Deionized water (DI water, resistance > 18.2 MΩ cm-1) was used for applications.

2. Characterization Methods

Powder X-ray diffraction (PXRD) patterns were collected on a Bruker D8 ADVANCE (German) equipped with Cu target, ceramic X-ray tube, 2.2kW, focal spot 0.4×12mm, goniometer radius 280 mm, minimum readable step size 0.0001deg.

Ultraviolet (UV) absorption data were obtained on a UV-1780 spectrophotometer. The fluorescence data were collected on a UV-1780 fluorescence spectrophotometer. The solid samples for the absorption and emission spectra were fixed between two quartz plates before measurements. All the PLQYs of the solid and liquid samples were determined by the quantum efficiency measurement system Edinburgh FLS980 at 25 °C under air. Time-resolved fluorescence measurements were conducted on a Edinburgh FLS980 at 25 °C under air. Raman spectra were obtained on a DXR2xi Raman imaging Microscope (DXR2xi, USA). FTIR spectra were conducted on a Spectrum Frontier FTIR spectrometer Bruker VERTEX70 made in Germany. Transmission electron microscopy (TEM) was carried on a JEM-2100 (JEOL Ltd., Japan) with an accelerating voltage of 200 kV. Fluorescence microscopic images were captured on an Olympus BX43 inverted microscope system. The excitation wavelength was 365 nm with an exposure time of 1s when acquiring a photo. All the photographs were taken by an iPhone 12 Plus camera under the irradiation of a hand-held UV lamp light (on/off).

3. Preparations

Preparation of Phe-OFN co-assemblies. OFN was employed as the molecular lighter to co-assemble with Phe, respectively. Firstly, Phe-OFN co-assemble single crystals for SCXRD analysis were prepared via solvent-evaporation,where THF was used as the solvent that can well dissolve Phe/OFN. Specifically, THF solutions (10 mg mL^{-1}, 1 mL) of Phe with an arene/OFN mole ratio of 1:1 were prepared. These solutions were further left to stand for several days to remove THF via slow evaporation, generating needle-like Phe-OFN single crystals with millimeter scale.

Secondly, micro-scale Phe-OFN crystals for fluorescence microscope (FM) and TEM observation were prepared via good solvent volatilization and poor solvent diffusion method. Phe and OFN were dissolved in 3 mL tetrahydrofuran at the molar ratio of 1:1, and volatilized for 3days, Phe-OFN microcrystals could be prepared for use. Phe were dissolved in 1mL tetrahydrofuran bottle at the molar ratio of 1:1, and 3mL methanol was added to the larger empty bottle.

Preparation of the FRET complexes.

Powder samples of the FRET complexes Phe-OFN@BPA-OFN and BPA-OFN@BPN-OFN were easily prepared via the two-step grinding. The specific steps are as follows:

First, 450 mg of Phe and OFN (Phe-OFN has a molar ratio of 1:1) were placed in an agate mortar, 0.02 mL of tetrahydrofuran (THF) was added, and ground for 10 seconds. Subsequently, 0.04 mL of THF was added to the resulting powder and grinding continued for 10 seconds to obtain Phe-OFN powder. Next, THF solutions of BPN-OFN in different volumes (0.01, 0.02 mL) (at a concentration of 2 mg mL-1 with a molar ratio of 1:1 for BPA-OFN) were added to the Phe-OFN powder, respectively, and ground again to finally obtain the target FRET complex. The molar percentage of BPA-OFN in these complexes is 0.2% and 0.4%, respectively.

Then, 650 mg of BPA and OFN (1:1 molar ratio for BPA-OFN) were placed in an onyx mortar, 0.02 mL of tetrahydrofuran (THF) was added, and ground for 10 seconds. Subsequently, 0.04 mL of THF was added to the resulting powder and grinding continued for 10 seconds to obtain BPA-OFN powder. Next, different volumes (0.05,

0.55, 3 mL) of BPN-OFN THF solution (at a concentration of 2 mg mL-1 with a molar ratio of 1:1 for BPN-OFN) were added to the BPA-OFN powder, respectively, and ground again to obtain the target FRET complex. The molar percentages of BPN-OFN in these complexes are 0.4%, 3.2%, and 20.8%, respectively.

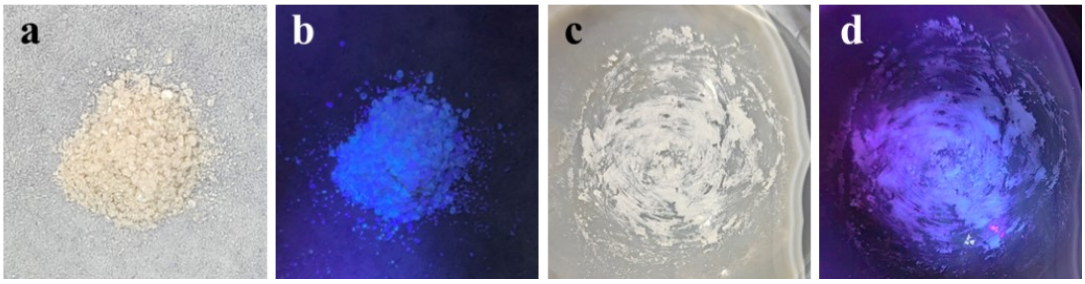

Figure S1. Photographs of Phe (a, b) and Phe-OFN powders (c, d) under daylight (a, c) and UV light irradiation (b, d), respectively.

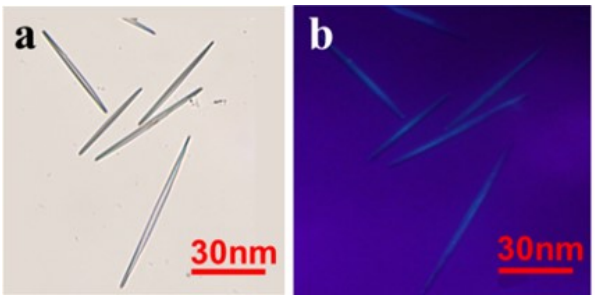

Figure S2. FM images of Phe crystal under daylight (a) and UV light irradiation (b), respectively.

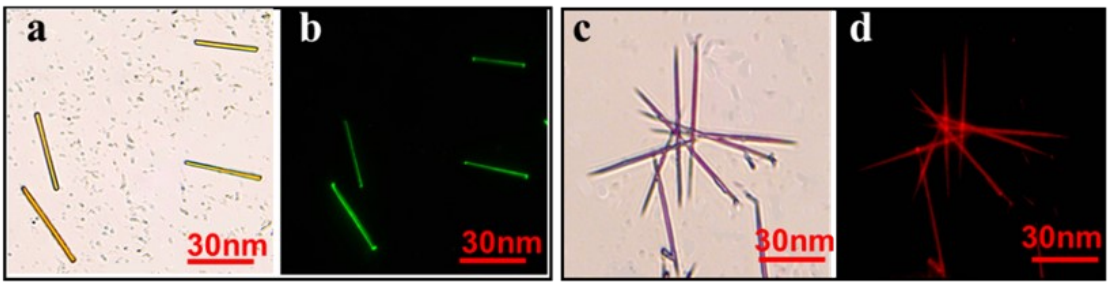

Figure S3. FM images of BPA-OFN crystal (a, b) and BPN-OFN crystal (c, d) under daylight (a, c) and UV light irradiation (b, d), respectively.

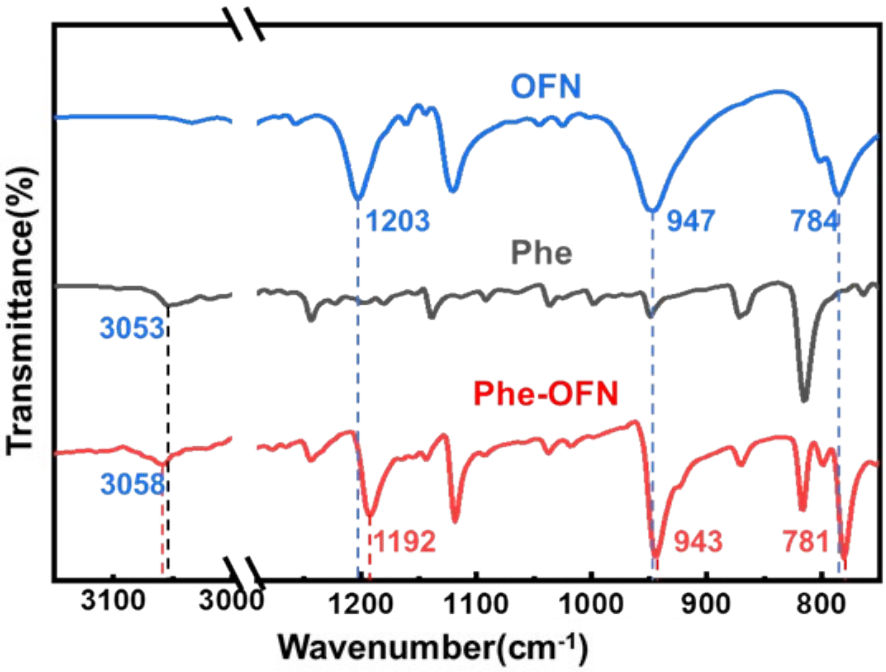

Figure S4. FTIR spectra of OFN, Phe and Phe-OFN, respectively. The appearance of the characteristic peaks at 781 cm^{-1} and 943 cm^{-1} from OFN (the stretching of C-F [1]) in the spectra of TC-OFN suggested the successful formation of Phe-OFN cocrystal. Besides, the stretching peak of OFN at 1203 cm^{-1} shifted to 1192 cm^{-1} after stacking with electron-rich Phe.[2] After being doped with electron-deficient OFN, the strong absorption bands at 3053 cm-1 (the stretching of Ar-H in TC) of Phe shifted to 3058 cm-1, which further confirmed the successful co-crystallization of Phe and OFN.

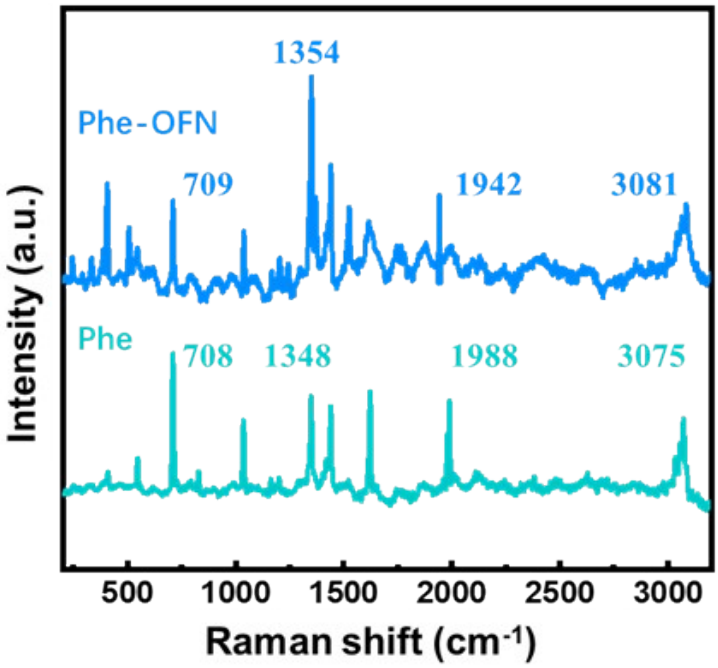

Figure S5. Raman spectra of Phe and Phe-OFN, respectively. The peaks at 1348 cm^{-1} and 3075 cm^{-1} from Phe shifted to 1354 cm^{-1} and 3081 cm^{-1} after forming cocrystal, respectively, indicating the decreased electron density of Phe molecules in the Phe-

OFN cocrystal.[1,2]

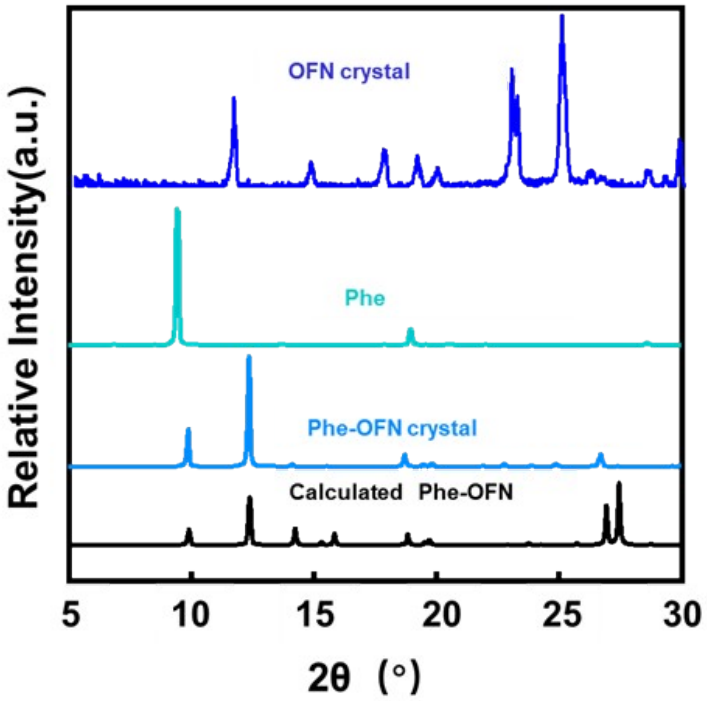

Figure S6. Experimental and calculated PXRD spectra of Phe-OFN cocrystal as well as the experimental PXRD spectra of OFN and Phe, respectively. The experimental PXRD result demonstrates the same pattern as the calculated one resulted from the single-crystal structure of Phe-OFN (CCDC number, 157248).

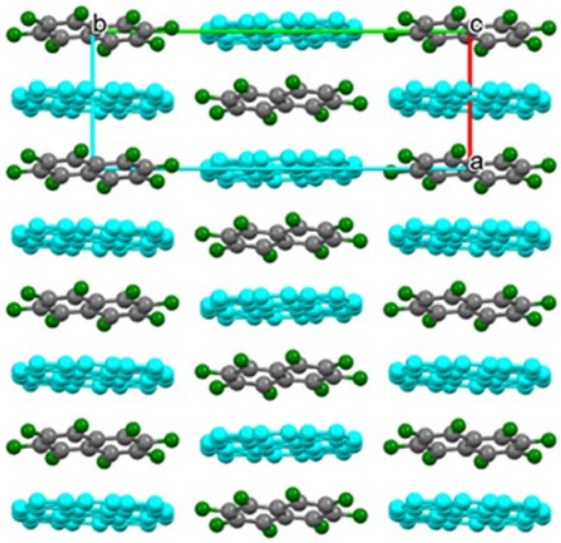

Figure S7. Packing structure of Phe-OFN (mole ratio of Phe/OFN = 1:1, CCDC number, 157248), which shows a mixed stacking mode.

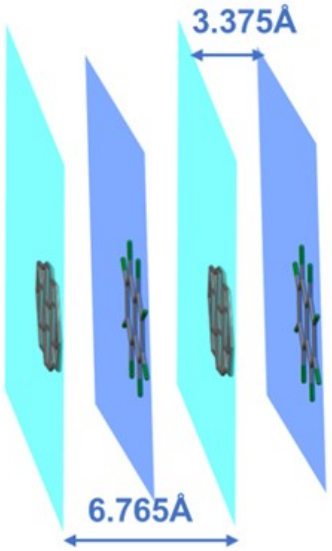

Figure S8. The distances between two Phe planes in Phe-OFN cocrystals. The distances between two Phe planes in Phe-OFN cocrystals, obtained from Diamond software. The intercalation of OFN molecules shoved the two adjacent Phe molecules and increased the distances to 6.765 Å.

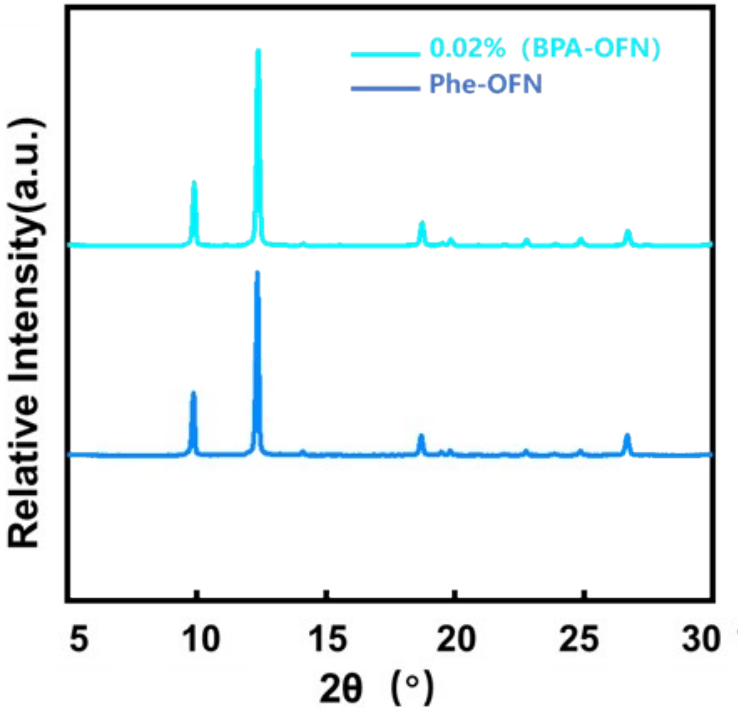

Figure S9. The corresponding PXRD spectra. The XRD image of powder containing 0.2% BPA-OFN is almost identical to that of pure Phe-OFN powder, indicating that the incorporation of BPA-OFN does not affect the crystal structure of Phe-OFN.

As demonstrated in the fluorescence microscope (FM) images, pure Phe–OFN microrod emits blue luminescence, and the doped FRET microrods exhibit uniform and tunable emission changing from cyan through green, yellow, orange and eventually to red, with increasing the doping ratio of BPA-OFN and BPN-OFN (Figure 5c). These observations are consistent with the results of the corresponding powders (Figure 5b). The color coordinate values in the CIE chromaticity diagram of the FRET samples were calculated from their PL spectra, i.e., (0.15,0.16),(0.18,0.31),(0.24,0.38),(0.36, 0.53), (0.42, 0.53), (0.46, 0.52), (0.50, 0.49), and (0.63, 0.37), respectively, which are consistent with the experimental results.

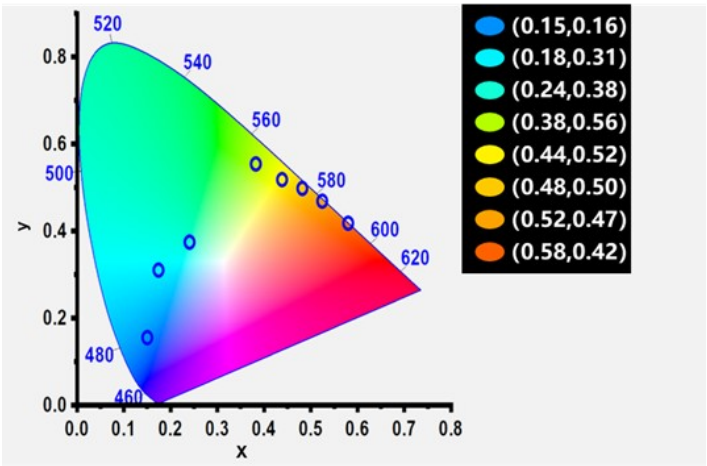

Figure S10. CIE coordinate values of the eight FRET samples.

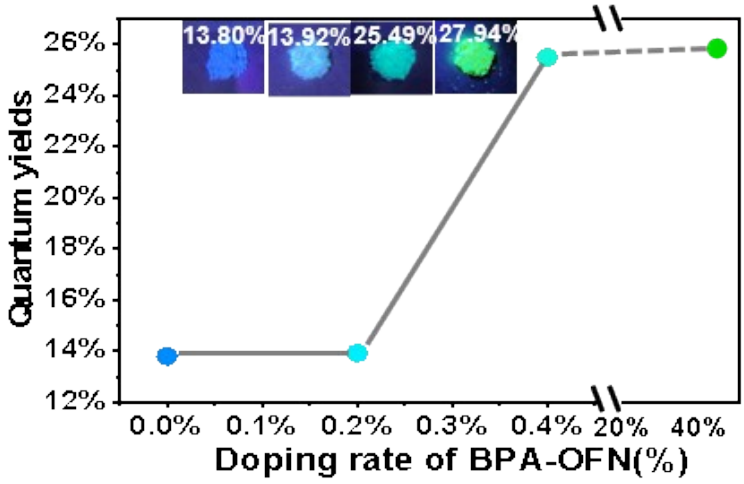

Figure S11. The curve of PLQY values of Phe-OFN@BPA-OFN with different doping

ratios of BPA-OFN.

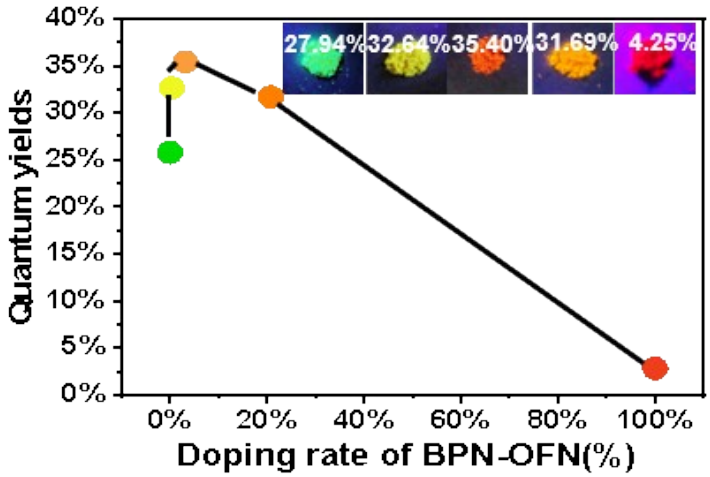

Figure S12. The curve of PLQY values of Phe-OFN@BPA-OFN@BPN-OFN with different doping ratios of BPN-OFN.

The mean fluorescence lifetimes can be calculated according to formula (1):

$$\tau = \sum T_i B_i \qquad (1)$$

In Formula 1, Ki represents the fitting constant, and Ti represents the lifetime value in different decay models.

Table S1. Ki, Bi, and τ values of Phe, Phe-OFN@BPA-OFN FRET complexes.

Sample	T_1（ns）	B_1（%）	T_2（ns）	B_2（%）	τ（ns）
Phe	1.3097	52.19	14.9679	47.81	7.87
Phe-OFN	1.6172	79.81	16.3100	20.19	4.56
$FRET_{0.2\%}$	1.6571	85.83	16.5916	14.17	3.75
BPA-OFN	17.3676	78.56	13.0305	21.44	16.44

Table S2. Ki, Bi, and τ values of BPA-OFN@BPN-OFN FRET complexes.

Sample	T_1（ns）	B_1（%）	T_2（ns）	B_2（%）	τ（ns）
BPA-OFN	17.3676	78.56	13.0305	21.44	16.44
$FRET_{0.4\%}$	14.3440	84.68	18.6821	15.32	15.01

$FRET_{3.2\%}$	14.3194	81.33	10.2024	18.67	13.55
$FRET_{20.8\%}$	8.2023	74.34	18.2477	25.66	10.78
BPN-OFN	1.6358	61.04	1.8818	38.96	1.73

Reference

1. G. R. Hanson, P. Jensen, J. McMurtrie, L. Rintoul and A.S, *Micallef. Chem. - Eur. J.,* 2009,**15**, 4156-4164.

2. Y. Kenji, M. Shiro. *Chem. Soc. Jpn*., 1980, **53**, 1949-1955.